Description and prediction of pesticide leaching

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A sound understanding of the factors affecting the mobility of pesticides in soil is an essential prerequisite to the development of functions which can accurately represent the array of processes which pesticides may undergo in soils. This requires detailed investigations on equilibrium and kinetic aspects of the sorption and desorption involved, the nature, extent and rate of any chemical transformation or biological degradation, and the roles of convection, diffusion and dispersion in the mobility of the pesticides in relevant soil structures. While a substantial amount of data is available on the interactions of pesticide chemicals with soil constituents, much of this has been obtained overseas. Also, the effects on these processes of soil properties, such as texture, clay mineral species, organic matter content, pH, salts and solvents present, need to be measured in detail for a much wider range of local soil-pesticide combinations in Australia. In particular, the significance of sorption time-dependency and long-term reversibility of sorption on the mobility of pesticides and the effects of soil environment on the rates of degradation under natural leaching conditions in the field remain poorly understood. The literature contains a multiplicity of predictive models varying greatly in terms of their complexity and claimed applicability. There is an urgent need to define the degree of complexity with which fundamental processes are treated in such models and the extent of characterisation of the range of physical, chemical and biological mechanisms required to avoid problems of site specificity and to provide a satisfactory database for predictive modelling. The development of practical methodologies, both for simulation modelling and compatible data collection, is essential.

Introduction

Pesticides play a vital role in maintaining adequate food quality and quantity. Total sales of pesticides in Australia increased nearly six fold to some $A 530 million during the last ten years, and it is estimated that the benefit of pesticide use to the Australian economy is as high as $A 4.5 billion. However, as a result of the massive use of pesticides in horticulture, and to a lesser extent in agriculture, there is increasing concern at the extent to which these chemicals may contaminate surface and groundwaters.

In the near future, both Federal and State Governments will be required to legislate or to act on existing legislation (such as the Soil and Water Conservation or Health Acts,) to restrict landholders and industry from discharging pollutants. A sound basis for understanding the potential hazards to water quality posed by the various chemicals concerned is essential in implementing such legislation.

As the expanding water catchment areas frequently involve areas of past, present or future horticultural use, the environmental challenge per unit area of land from pesticide use in horticulture is exceptionally high, particularly when such waters are also exploited for domestic uses (e.g. the Riverland areas of South Australia, the Sunraysia area of Victoria, the Murrumbidgee Irrigation area and Richmond River Valley of NSW, and the Pemberton–Manjimup and Ord River irrigation areas of Western Australia). In addition, there are numerous small catchment areas around several capital cities in close proximity to horticultural activities.

Systemic monitoring studies of pesticides in groundwaters are lacking. However, a recent report (EPA, 1989) indicated that an increasing number of samples, with levels of organochlorine pesticides exceeding EPA criteria, have been obtained from groundwaters in Western Australia. Similarly, increasing levels of the pesticides have also been found in river and estuarine waters of Western Australia. It is significant that under horticultural areas in Australia,

very high levels of nitrates (up to 8 times the permissible limit) have been found in some groundwaters (Pionke & others, 1990). In a horticultural catchment in South Australia (Piccadilly Valley), some 83% of surface water and 100% of sediment samples tested were found to contain pesticide residues (Thoma, 1990). Stadter & others (1992) have similarly reported the presence of atrazine and simazine in groundwaters in South Australia. The detection by 1988 of some 73 pesticides in groundwaters of various states in the USA has induced a massive research effort on pesticide–soil interactions in that country. A recently conducted preliminary survey of groundwater contamination from various sources in Australia (Jacobson & Lau, 1988) recommended that evaluation of non-point source pollution from herbicides and pesticides is urgently required.

While it is relatively easy to enunciate the objectives of a comprehensive research program to understand the factors determining pesticide leaching, the development of practical methodologies for simulation and predictive modelling and compatible data collection pose many problems requiring integration and rationalisation of input from soil scientists, industrial chemists and hydrologists. This paper provides a brief review of the major aspects of concern and the work recently undertaken at the University of Western Australia under funding provided by the AWRAC and LWRRDC.

Pesticide mobility

The large number of pesticides currently in use include a wide variety of compounds differing markedly in both their physical and chemical properties, i.e. whether ionic or non-ionic, weakly acidic or basic, hydrophobic or hydrophilic. The ionic pesticides include both cationic (e.g. paraquat, diquat) as well as anionic (2,4-D). They differ greatly in their aqueous solubility and volatility, i.e. from highly soluble and non-volatile (e.g. paraquat) to sparingly soluble and highly volatile (e.g. trifluralin). When pesticides enter the soil, they are subjected to a variety of physical, chemical and biological processes including sorption–desorption, chemical transformation and biological degradation. Previous studies here and elsewhere have shown that the retention and release processes for pesticides are not only directly related to their chemical nature, but also to the nature and properties of the soil and its

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constituents (Singh & others, 1988a,b; Kookana & Aylmore, 1993a)). Soils vary tremendously in their composition, physical structure and chemical environment. While substantial data on pesticide/soil interactions are available, much of this has been obtained overseas and work here (Singh & others, 1988a) has demonstrated that the effects on these processes of soil properties (such as texture, clay mineral species, organic matter content, pH, salts and solvents present, etc.) need to be measured in detail for a much wider range of local soil–pesticide combinations.

Sorption-desorption processes

Sorption of pesticides by soil is undoubtedly one of the major processes influencing their accessibility to target organisms and their potential to reach non-target organisms by leaching to groundwater. Sorption may result in decreasing biological activity with respect to the target organism, in enhanced degradation of the pesticide before leaching and in retardation in movement with leaching solutions (Weed & Weber, 1974). Organic matter and clay minerals are undoubtedly the major constituents in determining the extent of sorption in soils and numerous studies on pesticide sorption have been reported including both inorganic and organic surface interactions (reviewed by Bailey & White, 1970; Weber, 1972; Weed & Weber, 1974; Calvet, 1980; Koskinen & Harper, 1990). Interactions of pesticides with model materials, such as homoionic clays and ion exchange resins, have been widely studied as these well-defined systems allow clearer elucidation of mechanisms and specific interactions (Mortland, 1970). However, in natural soils the interactions can be expected to be much more complex than in pure materials (Hamaker & Thompson, 1972). Kookana & Aylmore (1993a) found that the sorption of cationic diquat and paraquat in some Western Australian soils followed the order of clay content in the soils and that both the type and contents of clay minerals present in the soil were important for sorption and subsequent desorption of the dipyridylium herbicides. For some other pesticides, in particular non-ionic compounds, the amounts sorbed were more directly related to organic matter contents than to clay contents (Singh & others, 1989; Aylmore & others, 1989). However, comparisons between data obtained on Australian soils with those for other world soils (Singh & others, 1990b) have demonstrated that substantial variation occurs, for example, in the adsorption of linuron and fenamiphos per unit weight of organic matter (K_{OM}), not only between soils from different regions but also between soils from the same region, clearly indicating that organic matter in Australian soils can behave quite differently in terms of the retention of pesticides.

In recent decades, various approaches have been used to describe solute–soil interactions. Considerable attention has been given to adsorption models based on gas-solid interactions that lead to Langmuir and Freundlich-type equations. These have sometimes been criticized for neglecting the generally electrostatic nature of the ion-soil interactions and for ignoring the heterogeneity of the surface adsorption energy. Preference has often been given to models based on the diffuse double layer (DDL) theories (Bowden & others 1974). In its complete form, the DDL adsorption model of Bowden & others (1974) requires five simultaneous equations that have to be solved by iterative procedures to estimate the equilibrium distribution of ions between solution and solid (adsorbed) phases. However, such complexity, while requiring large computational time, brings little useful refinement in the simulation of break-

through curves (Murali & Aylmore, 1981). Singh & others (1988b) found that sorption data for fenamiphos, linuron and simazine could readily be fitted to a Freundlich-type equation, while that for Diquat more closely fitted the Langmuir equation. As discussed later it has become increasingly clear that the kinetic aspects of the sorption processes need to be considered when dealing with solute transport.

While the organic matter and clay contents of a soil are undoubtedly the main substrates for pesticide sorption (Hamaker & Thompson, 1972; Weed & Weber, 1974; Green, 1974; Koskinen & Harper, 1990) the extent and reversibility of these interactions can be greatly influenced by other factors such as pH, soil solute concentration or the presence of organic cosolvents and competitive ions (Kookana & others, 1989; Singh & others 1988b).

Effect of pH

Both organic matter and clays have pH-dependent charges and hence their ion exchange capacies change with pH. The relative quantities of basic and acidic pesticide in ionic form are also dependent on the pH of the system. Organobasic compounds (s-triazines) become cations at low pH and this results in increased sorption (Weber & others, 1969), wheras the acidic compounds are proton donors (2,4-D, dinoseb sulfonyl ureas) which at high pH (one or more pH units above the pKa of acid) become anions due to dissociation. The adsorption of simazine and to a lesser extent of linuron and fenamiphos, were shown to decrease with increasing pH in Western Australian soils varying in texture from sand to clay (Aylmore & others, 1989). Simazine is a weakly basic herbicide and has a pKa of 1.4. As the pH increases, the proportion of simazine cations in solution decreases and hence the adsorption decreases. In contrast to the weakly basic Simazine, the adsorptions of paraquat and diquat (both strongly cationic) were unaffected by change in pH (Singh & others, 1988a). Soil acidification, as a result of fertilization and cropping, is a major problem in many areas of Australia as elsewhere, and management practices (such as liming) can also play a significant role in determining the pH of a soil and hence pesticide sorption (Singh & others, 1988a). It has also been suggested that the pH at the surface of soil colloids can be up to two units lower than that measured in the soil solution (Hayes, 1970) and that the pH of rhizosphere soil may differ from that of bulk soil by up to 1 pH unit (Nye, 1986). Such effects clearly need to be considered in assessing pesticide-leaching potential.

Reversibility of sorption — hysteresis

The reversibility of sorption reactions plays a significant role in determining the behaviour of any pesticide in the soil profile. That is, whether the solid phase provides a permanent sink or merely a temporary reservoir, releasing the chemical back into solution in response to a decrease in solution concentration. Numerous workers (Swanson & Dutt, 1973; van Genuchten & Wierenga, 1974; Bowman & Sans, 1977; Rao & others, 1978; Koskinen & Cheng, 1979; Di Toro & Horzempa, 1982; Brusseau & Rao, 1989; among others) have reported that the sorption–desorption reaction was non-singular. Hysteresis has frequently been observed in the sorption–desorption isotherms for pesticides [(e.g. atrazine; Swanson & Dutt, 1973); picloram (van Genuchten & others, 1974); diuron (Peck & others, 1980); 2,4,5-T (van Genuchten & others, 1977); parathion (Bowman & Sans, 1985); linuron, simazine (Singh & others, 1990)]. The

mechanisms underlying measurements of apparent hysteresis appear many and varied, sometimes being attributed to experimental artifacts, such as changes in sorption capacity arising from shaking and centrifugation, incomplete equilibration, the presence of 'implicit sorbate' altering competitive sorption, as well as degradation or transformation of the pesticide during longer term experiments. However, true hysteresis as a result of the entrapment of pesticides in the organic matter matrix (Ogner & Schnitzer, 1971; Johnson & Starr, 1972; Khan, 1978; Burchill & others, 1981; Kookana & others, 1990) or within mineral particles (McCloskey & Bayer, 1987) seems likely to occur (Singh & others, 1990b). This is an important consideration since the effects of various factors, such as soil solution concentration and organic cosolvents on the extent of hysteresis and ease of desorption, have been shown to have serious implications for the mobility of pesticides in soil profiles (Singh & others, 1990b, Kookana & Aylmore, 1993b).

Effect of competitive species

Competition for sorption sites by other inorganic and organic compounds present in the solution can modify the behaviour of pesticides in the soil. Inorganic cations compete directly with cationic and cationizable pesticides and reduce their sorption (Weber & Weed, 1968; Hance, 1969; Best & others, 1972; Hayes & others, 1975). Increases in the salt concentration of the soil solution (from 0.005 to 0.05 M $CaCl_2$) were observed to result in decreases in sorption capacities for diquat and paraquat herbicides ranging from some 17% for a sandy soil to 40% for a clay soil (Kookana & Aylmore, 1993a). Desorption of the herbicides was also significantly enhanced by increase in the salt concentration, indicating that the herbicides were less strongly held. Both Ca^{2+} and Na^+ competed with the herbicides for the sorption sites but Na^+ was not as effective as Ca^{2+}. While pesticides, such as diquat and paraquat, are generally considered to be essentially irreversibly retained by soil, it is significant that some 60% of adsorbed diquat could be released to solution from a loamy sand soil by extraction with 0.05 M $CaCl_2$. In contrast, the adsorption of linuron, simazine and fenamiphos were only slightly decreased by increasing soil solution concentration (Singh & others, 1988a,b).

Effect of organic cosolvent

Interest in the behaviour of pesticides in soils in the presence of organic cosolvents arises from possible implications with respect to the transport of pesticides and other organic solutes in any situation where organic solvents may be involved, e.g. at waste disposal sites, at land treatment sites for concentrated wastes containing solvents, and in cases of accidental spills. In addition, it is common practice among workers to use pesticide stock solutions prepared in organic solvents for sorption studies (Calvet, 1980), particularly for pesticides having low aqueous solubility (Dunigan & McIntosh, 1971). Recent studies (Singh & others, 1990) have shown that the adsorption and desorption behaviour of the pesticides linuron and simazine are both significantly affected by the presence of methanol. Adsorption of the herbicides decreased with increasing methanol content of the water/methanol mixture and followed the solvophobic theory, which describes the adsorption of hydrophobic organic compounds in soils. Hysteresis, observed after desorption in $CaCl_2$ solution, decreased with increasing methanol content for both herbicides. The decrease in hysteresis was attributed to the swelling of the organic matter and the accompanying increased accessibility to solutes. In addition to their direct effect on adsorption, increased reversibility of the adsorption process (i.e. less hysteresis) in the presence of organic solvents, will obviously increase the mobility of a pesticide in the soil profile. At 10% methanol content, the retardation factor (R) for these herbicides decreased to almost half the value in aqueous solution. The presence of methanol at levels of 50% and 60% of solvent mixture, decreased R for simazine and linuron by factors of 10 and 12 respectively (Singh & others, 1990).

Degradation

Whether a pesticide persists for a long time or is rapidly degraded in soil is also a major determinant of the extent to which it can pose a pollution hazard. Those that degrade rapidly are less exposed to leaching effects, since the rate of degradation to their metabolites will determine the residence times of the parent compounds in the soil profile. However, for certain pesticides the degradation process leads to the formation of metabolites which are themselves equally, or more toxic than the parent compound, thus maintaining or even increasing the potential hazard to groundwater (e.g. fenamiphos nematicide which transforms to its sulfoxide and sulfone). The significance of these processes in soils under Australian climatic conditions is poorly understood (Ferris & Haigh, 1992). The role of other factors, such as organic matter, moisture content and temperature in the degradation process, also need to be investigated. In the field, temperature is a function of depth in a soil profile, and hence may be of considerable importance in controlling pesticide degradation and susceptibility to leaching.

Sorption time-dependency

The kinetics of pesticide sorption in soil has until recently received relatively little experimental attention, and most sorption studies on pesticides in soil have dealt with equilibrium aspects (Rao & Jessup, 1983; Yaron & others 1985). Much previous work has been limited to the measurement of sorption equilibrium by batch methods involving shaking or stirring of soil suspensions. Consequently, studies of pesticide sorption by batch methods have frequently indicated that the major fraction of pesticide sorption in soil is essentially instantaneous. However, there is substantial evidence from breakthrough curves involving flow in soil columns, that the sorption process is almost invariably time dependent under the flow conditions (Murali & Aylmore, 1980; Kookana & others, 1991). Recent studies have confirmed the time-dependency of sorption in the field (Pignatello, 1990; Brusseau & others, 1991). The effects of such sorption dynamics may arise both from structural limitations on diffusion into micropores as well as from the kinetics of the sorption process itself. Acceptance of an invalid instantaneous reaction could clearly lead to serious underestimation of potential leaching and transport of a pesticide to groundwater (Kookana & others, 1991). Flow techniques, such as that developed by Kookana & others (1991), are preferable over batch techniques (Sparks, 1985) for estimating relevant parameters because these are realistic and suitable for modelling transport of pesticides in soil profiles.

Modelling of pesticide sorption and transport

Numerous mathematical models for describing and predicting the transport of non-reactive and reactive solutes, such as pesticides under saturated as well as unsaturated flow conditions, have been developed in recent decades. Common models of organic chemical transport and their strengths and weaknesses have recently been reviewed by Gallant & Moore (1991) and by Parthapar & Bowmer (1991). Such models can be broadly divided into two classes on the basis of the degree of complexity with which fundamental processes are incorporated and the extent of characterisation of the range of physical, chemical and biological factors required. Recent reviews of mechanistic or process-based models employing the classical convection–diffusion–dispersion equations have been provided by different workers (van Genuchten, 1991; Jury & Ghodrati, 1989; Brusseau & Rao, 1989). The development of mechanistic models and their evaluation under controlled laboratory conditions provides important insights into the significance of the various physical and chemical processes involved in determining pesticide movement in soils (research oriented). However, the complexity attendant on the multiplicity of factors frequently operating in the field, is likely to make such models extremely cumbersome and of restricted applicability. In contrast, models based on stochastic representation of the transport properties (Jury & others, 1987; Rao & Jessup, 1983) provide little understanding of the underlying physical and chemical processes and seek a more functional description in terms of readily accessible parameters (i.e. management oriented). Despite this simplification, functional models often give simulations that are at least as good as those of mechanistic models (e.g. Nicholls & others, 1982; De Willigen, 1991) while using far less computer time. They seem likely to be increasingly advantageous as the physical scale of the modelling exercise increases (Addiscott, 1992).

Independant measurement of parameters under realistic conditions

In solute transport studies, a number of different rate laws describing the time dependency of the sorption reaction in soils have been used with varying degrees of success. These include simple one-site linear or non-linear kinetic models, two-site sorption models and several others (reviewed by Nielsen & others, 1986; Brusseau & Rao, 1989). More recently, Boesten (1987) used a three-site kinetic model, and Selim & Amacher (1988) a second-order two-site kinetic model in their solute transport studies. Experimental evidence of such kinetic reactions have been obtained in a few studies only and even then by the batch technique. Since substantial differences in sorption between flow and batch systems have frequently been noted (e.g. Ardakani & McLaren, 1977; Wagenet & others, 1977; Gaber & others, 1992), it is essential that sorption rate coefficients be obtained under flow conditions for such transport studies. The peak maxima method applied to breakthrough curves (BTCs) is commonly used in the chromatography literature for the determination of a distribution isotherm (Huber & Gerritse, 1971). By comparing the BTCs for a pesticide for different amounts of pesticide injected into a soil column with those for a non-retarded solute, it is possible (Kookana & others 1992b) to obtain a series of sorption values corresponding to different solution concentrations at a given rate of flow

or residence time. When the flow rates employed are slow enough to allow solute to react completely with the soil, such sorption values will represent an equilibrium sorption isotherm comparable with those obtained by batch methods, at least in principle. However, at higher rates the sorption values will represent dynamic distribution isotherms. The residence time of a pesticide in the soil column can be varied by changing the flow rate of the solution entering the soil columns. In practice, the sorption values versus residence times obtained from the sets of BTCs at different rates of flow, are equivalent to the set of sorption versus equilibration-time data obtained by the batch method. This sorption versus time data can then simply be subjected to various rate laws, such as the first-order kinetic equation, and the rate parameters can be calculated.

Kookana & others (1992a) used this flow technique to study the sorption kinetics of three pesticides in laboratory studies on four Western Australian soils. Sorption data of all pesticides showed an initial rapid rate followed by a slower rate of sorption. While a first-order equation failed to satisfactorily describe the sorption data, both the Freundlich two-site kinetic equation and the parabolic diffusion law fitted well to the data. The rapid component of sorption varied from 0 to 25% of total sorption (24 h sorption value) for the various pesticides. A comparison of sorption data obtained by a batch technique and a flow technique revealed that sorption occurs at a much faster rate under batch conditions, presumably because of shaking and the high solution to soil ratio. Under the batch conditions, the instantaneous component of sorption was very high (up to 90% of 24 h sorption value). The characteristics of the soil also affected the rate of sorption of the pesticides. A well-structured soil with high organic matter content showed a slower rate of sorption compared with a dispersed soil with low organic matter. Although time-dependency of sorption is demonstrably a fact in practical situations, the extent to which it plays a significant role and needs to be accounted for in determining the overall leaching of pesticides in the field where water infiltration and redistribution generally follow a stop/go scenario remains to be established.

For the most effective pesticide usage and rapid assessment of their likely pollution potential at any given location, management models need to be designed requiring the minimum number of parameters while effective and with structures that can be readily modified for site specific purposes. Kookana & Aylmore (1993b) examined the groundwater pollution potentials predicted for a number of pesticides and the influence of organic matter distribution by calculating the mass of pesticides leaching past the zone of maximum sorption and biological activity in a sandy soil profile of the Swan Coastal Plain, W.A., using a simple screening model (Jury & others, 1987). Hydrological parameters were estimated from local soil and climatic data, and in the absence of local data sorption (Koc) and degradation (half-life) parameters were obtained from the literature. Assuming a uniform OM content, the model predicted that of 40 pesticides evaluated, 20 have the potential to reach groundwater in significant amounts (>0.1% of applied mass). However, when an exponentially decreasing OM content with depth in the soil profile was incorporated in the model, the number of pesticides reaching groundwater increased to 30 and the residual concentrations were dramatically increased. The use of local Koc and half-life values for seven pesticides, yielded substantially different residual concentrations to those obtained on the basis of literature values, emphasising the

need for site specific data. A clearer understanding of the extent to which the neglect of factors (such as dispersion and diffusion, sorption non-equilibrium, water repellancy and prefential flow paths, hysteresis and the use of average recharge rates), will lead to significant over- or under-estimation of pollution potentials is vital to the development of effective and practical management models.

Although the individual mechanisms involved in transport have been extensively studied and modelled in isolation, it is of particular importance to develop predictive capabilities of their integrated consequences. While the different aspects are most readily characterized under controlled laboratory conditions, extrapolation to field conditions is invariably complicated by climatic and other variables. In particular, the structure of the soil plays an important part in the leaching process. Although some progress has been made in characterising soil structure (Dexter, 1988), little success has been achieved in relating water movement, and hence solute transport, to pore size distribution and continuity. While predictive models provide important tools in both research and management, comprehensive field data sets on pesticide transport and volatilization remain needed to accurately assess and improve the performance of these models. There is an urgent need to define the degree of complexity with which fundamental processes need to be treated in such models as well as the extent of characterisation of the variety of physical, chemical and biological parameters required in order to avoid problems of site specificity and to provide an effective approach to defining the potential hazard posed by particular pesticide/soil combinations. Improved technologies for measuring pesticide transport and degradation processes in heterogeneous field soils are also needed.

References

Addiscott, T.M., 1992 — Simulation modelling and soil behaviour. *Proceedings International Society Soil Science Symposium on "Operational Methods to Characterise Soil Behaviour in Space and Time., Cornell University, Ithaca, July.*

Ardakani, M.S. & McLaren, A.D., 1977 — Absence of local equilibrium during ammonia transport in a soil column. *Soil Science Society of America Journal*, 41, 677–679.

Aylmore, L.A.G., Singh, Rai & Gerritse, R.G., 1989 — Adsorption–desorption behaviour of pesticides and implications for groundwater pollution. *Water 89 Inter. Conf., Bangkok, Thailand.* EQM, 4–9.

Bailey, G.W. & White, J.L., 1970 — Factors influencing the adsorption, desorption and movement of pesticides in soils. *Residue Reviews*, 32, 29–92.

Best, J.A., Weber, J.B. & Weed, S.B., 1972 — Competitive adsorption of Diquat^{2+}, Paraquat^{2+}, and Ca^{2+} on organic matter and exchange resins. *Soil Science* 114, 444–450.

Bowden, J.W., Posner, A.M. & Quirk, J.P., 1974 — A model for ion adsorption on variable charge surfaces. *Transactions 10th International Congress Soil Science, Moscow*, 2, 29–36.

Boesten, J.J.T.I., 1987 — Modelling pesticide transport with a three site sorption sub-model: a field test. *Netherlands Journal of Agricultural Science*, 35, 315–324.

Bowman, B.T. & Sans, W.W., 1985 — Partitioning behaviour of insecticides in soil-water systems. II. Desorption hysteresis effects. *Journal of Environmental Quality*, 14, 270–273.

Burchill, S., Hayes, M.H.B. & Greenland, D.J., 1981 —

Adsorption. *In* Greenland, D.J. & Hayes, M.H.B. (editors),The Chemistry of Soil Processes. *John Wiley & Sons Ltd*, 221–400.

Brusseau, M.L. & Rao, P.S.C., 1989 — Sorption nonideality during organic contaminant transport in porous media. *CRC Critical Reviews in Environmental Control*, 19, 33–99.

Brusseau, M.L., Jessup, R.E. & Rao, P.S.C., 1991 — Nonequilibrium sorption of organic chemicals. *Environmental Science and Technology*, 25, 134–142.

Calvet, R., 1980 — Adsorption-desorption phenomena. *In* Hance, R.J. (editor), Interactions between herbicides and the soil. *Academic Press, London*, 1–30.

De Willigen, P., 1991 — Nitrogen turn-over in the soil-crop system: comparison of fourteen models. *Fertilizer Research*, 27, 141–149.

Dexter, A.R., 1988 — Advances in characterisation of soil structure. *Soil and Tillage Research*, 11, 199–238.

Di Toro, D.M. & Horzempa, L.M., 1982 — Reversible and resistant components of PCB adsorption-desorption: Isotherms. *Environmental Science and Technology*, 16, 594–602.

Dunigan, E.P. & MacIntosh, Th., 1971 — Atrazine — soil organic matter interaction. *Weed Science*, 19, 279–282.

EPA, 1989 — Monitoring Pesticides — A review. *The Environment Protection Authority, Perth, Western Australia, Bulletin* No. 407, pp 67.

Ferris, I.G. & Haigh, B.M., 1992 — Herbicide persistence and movement in Australian soils: Implications for agriculture. *In* Altman, J. (editor), Pesticide Interaction in Crop Production. *CRC Press* (in press).

Gaber, H.M., Comfort, S.D., Inskeep, W.P. & El-Attar, H.A., 1992 — A test of local equilibrium assumption for adsorption and transport of picloram. *Soil Science Society of America Journal*, 56, 1392–1400.

Gallant, J.C. & Moore, I.D., 1991 — Models of organic contaminant transport and degradation: A review. *In* Moore, I.D. (editor), Modelling the Fate of Chemicals in the Environment. *CRES, ANU, Canberra.* 22–39.

Green, R.E., 1974 — Pesticide-clay-water interactions. *In* Guenzi, W.D. (editor), Pesticides in soil and water. *Soil Science Society of America Inc. Publ., Madison*, 33–37.

Hayes, M.H.B., 1970 — Adsorption of triazine herbicides on soil organic matter, including a short review on soil organic chemistry. *Residue Reviews*, 32, 131–168.

Hayes, M.H.B., Pick, M.E. & Toms, B.A., 1975 — Interaction between clay minerals and bipyridylium herbicides. *Residue Reviews*, 57, 1–25.

Hamaker, J.W. & Thompson, J.M., 1972 — Adsorption. *In* Goring, C.A.I. & Hamaker, J.W. (editors), Organic Chemicals in the Soil Environment, Vol. 1. *Marcel Dekker Inc., N.Y.* 49–143.

Hance, R.J., 1969 — The influence of pH, exchangeable cation and the presence of organic matter on the adsorption of some herbicides by montmorillonite. *Canadian Journal of Soil Science*, 49, 357–364.

Huber, J.F.K. & Gerritse, R.G., 1971 — Evaluation of dynamic gas chromatographic methods for the determination of adsorption and solution isotherms. *Journal of Chromatography*, 58, 137–158.

Jacobson, G. & Lau, J.E., 1988 — Groundwater contamination incidents in Australia: An initial survey, *Bureau of Mineral Resources, Australia, Report* 287.

Johnson, R.E. & Starr, R.I., 1972 — Ultrarapid extraction of insecticides from soil using a new ultrasonic technique. *Journal of Agriculture and Food Chemistry*, 20, 48–51.

Jury, W.A. & Ghodrati, M., 1989 — Overview of organic chemical environmental fate and transfer modelling

approaches. *In* Reactions and Movement of Organic Chemicals in Soil. *Soil Science Society of America Journal Special Publication, 22, 271–304.*

Jury, W.A., Focth, D.D. & Farmer, W.J., 1987 — Evaluation of pesticide groundwater pollution potential from standard indicies of soil–chemical adsorption and biodegradation. *Journal of Environmental Quality*, 16, 422–428.

Khan, S.U., 1973 — Interaction of humic substances with bipyridylium herbicides. *Canadian Journal of Soil Science*, 53, 199–204.

Kookana, R.S. & Aylmore, L.A.G., 1993a — Retention and release of Diquat and Paraquat herbicides in soils, *Australian Journal of Soil Research*, 31, 97–109.

Kookana, R.S. & Aylmore, L.A.G., 1993b — Estimating groundwater pollution potential of pesticides. *Australian Journal of Soil Research* (in prep).

Kookana, R.S., Aylmore, L.A.G. & Gerritse, R.G., 1992a — Time dependent sorption of pesticides during transport in soils. *Soil Science,* 154, 214–225.

Kookana, R.S., Gerritse, R.G. & Aylmore, L.A.G., 1992b — A method for studying nonequilibrium sorption during transport of pesticides in soil. *Soil Science*, 154, 344–349.

Kookana, R.S., Schuller, R.D. & Aylmore, L.A.G., 1991 — Numerical simulation of pesticide transport measured in a sandy soil *In* Moore, I.D. (editor), Proceedings of Workshop on Modelling the fate of chemicals in the environment. *Centre for Resource and Environmental Studies, Canberra*, 75–82.

Kookana, R.S., Schuller, R.D. & Aylmore, L.A.G., 1992c — Simulation of simazine transport through soil columns using time-dependent sorption data measured under flow conditions. *Journal of Contaminant Hydrology, (*in press).

Koskinen, W.C. & Cheng, H.H., 1979 — Effects of experimental variables on 2,4,5-T adsorption–desorption in soil. *Journal of Environmental Quality,* 12, 325–330.

Koskinen, W.C. & Harper, S.S., 1990 — The retention process: mechanisms. *In* Cheng, H.H. (editor), Pesticides in the Soil Environment: Processes, Impacts and Modelling. *Soil Science Society of America Book Series* No. 2 51–78.

McCloskey, W.B. & Bayer, D.E., 1987 — Thermodynamics of fluridone adsorption and desorption on three Californian soils. *Soil Science Society of America Journal,* 51, 37–44.

Mortland, M.M., 1970 — Clay organic complexes and interactions. *Advances in Agronomy*, 22, 75–114.

Murali, V. & Aylmore, L.A.G., 1980 — No-flow equilibration and adsorption dynamics during ionic transport in soils. *Nature*, 283, 467–469.

Murali, V. & Aylmore, L.A.G., 1981 — Modelling adsorption in solute flow simulations: diffuse double layer versus gas-solid interaction approaches. *Soil Science*, 131, 76–81.

Nicholls, P.H., Bromilow, R.H. & Addiscott, T.M., 1982 — Measured and simulated behaviour of fluometuron, aldoxycarb and chloride ions in a structured soil. *Pesticide Science*, 13, 475–483.

Nielsen, D.R. van Gebuchten, M. Th. & Biggar, J.W., 1986 Water flow and solute transport processes in the unsaturated zone. *Water Resources Research*, 22, 89–108.

Nye, P.H., 1986 — Acid-base changes in the rhizosphere. *In* Advances In Plant Nutrition. *Praeger Scientific, N.Y.*, 129–154.

Ogner, G. & Schnitzer, M., 1971 — Chemistry of fulvic acid, a soil humic fraction, and its relation to lignin. *Canadian Journal of Chemistry*, 49, 1053–1063.

Parthapar, S.A. & Bowmer, K.H., 1991 — Pesticide issues in irrigation agriculture – Can modelling help. *In* Moore, I.D. (editor), Modelling the Fate of Chemicals in the Environment. *CRES, ANU, Canberra*, 9–12.

Peck, D.E., Corwin, D.L. & Farmer, W.J., 1980 — Adsorption desorption of diuron by freshwater sediments. *Journal of Environmental Quality*, 9, 101–106.

Pignatello, J.J., 1990 — Slowly reversible sorption of aliphatic hydrocarbons in soils II. Mechanistic aspects. *Environmental Toxicology and Chemistry*, 9, 1117–1126.

Pionke, H.B., Sharma, M.L. & Hosking, J.A., 1990 — Horticulturally cropping effects on groundwater quality in the Swan Coastal Plain. *CSIRO Division of Water Resources Series,* No. 2.

Rao, P.S.C. & Jessup, R.E., 1983 — Sorption and movement of pesticides and other toxic organic substances in soils. *In* Nelson, D.W., Tanji, K.J. & Elrick, D.E. (editors), Chemical Mobility and Reactivity in Soil Systems. *Soil Science Society of America Madison, Wisc.,* 183–201.

Rao, P.S.C., Davidson, J.M. & Kilcrease, D.P., 1978 — Examination of nonsingularity of adsorption-desorption isotherms for soil-pesticide systems. *Agronomy Abstracts* 34.

Selim, H.M. & Amacher, M.C., 1988 — A second-order kinetic approach for modelling solute retention and transport in soils. *Water Resources Research,* 24, 2061–2075.

Singh, Rai, Aylmore, L.A.G. & Gerritse, R.G., 1990 — Evaluation of potential for groundwater pollution by some pesticides in a deep sand of Western Australia. *Proceedings of National Workshop on Herbicide Persistence, Melbourne, Nov., 1989.*

Singh, R., Gerritse, R.G. & Aylmore, L.A.G., 1988 — Effect of soil conditions associated with management practices on the retention and release of pesticide. *Australian Society of Soil Science Conference, Merredin, W.A., August,* 119–123.

Singh, Rai, Gerritse, R.G. & Aylmore, L.A.G., 1988 — Physico-chemical interaction and mobility of pesticides in soils. *National Workshop on Persistence of Herbicide Residues in Wheat Cropping Systems in Australia, Melbourne, Oct.,* 32–47.

Singh, R., Gerritse, R.G. & Aylmore, L.A.G., 1990 — Adsorption-desorption behaviour of selected pesticides in some Western Australian soils. *Australian Journal of Soil Research,* 28, 227–243.

Singh, R., Gerritse, R.G. & Aylmore, L.A.G., 1990 — Effect of organic co-solvent on adsorption and desorption of Linuron and Simazine in soil. *Australian Journal of Soil Research,* 28, 717–725.

Sparks, D.L., 1985 — Kinetics of ionic reactions in clay minerals and soils. *Advances in Agronomy*, 38, 231–266.

Stadter, F.A., Emmett, A. & Dillon, P., 1992 — Occurrence of Atrazine in groundwater in the southeast of South Australia. Report of Stage 2 of Investigation, *CSIRO, Centre for Groundwater Studies Report*, No. 45.

Swanson, R.A. & Dutt, G.R., 1973 — Chemical and physical processes that affect atrazine and distribution in soils. *Soil Science Society of America Journal*, 37, 872–876.

Thoma, K., 1990 — Pilot survey of pesticides residues in streams draining horticultural catchment, Piccadilly Valley, South Australia. *South Australian Department of Agriculture, Adelaide.*

van Genuchten, M.Th., 1991 — Recent progress in

modelling water flow and chemical transport in the unsaturated zone. *In* Kienitz, G. & others (editors), Hydrological Interaction Between Atmosphere, Soil and Vegetation. *IAHS Publ.* No. 204, *Institute of Hydrology, Wallingford, Oxfordshire, U.K.* 169–183.

van Genuchten, M.Th., Wierenga, P.J. & O'Connor, G.A., 1977 — Mass transfer studies in sorbing porous media: III. Experimental evaluation with 2,4,5-T. *Soil Science Society of America Journal,* 41, 278–285.

van Genuchten, M.Th. & Wierenga, P.J., 1974 — Simulations of one-dimensional solute transport in porous media. *New Mexico Agricultural Experimental Station Bulletin* 628.

van Genuchten, M.Th., Davidson, J.M. & Wierenga, P.J., 1974 — An evaluation of kinetic and equilibrium equation for the prediction of pesticide movement through porous media. *Soil Science Society of America Proceedings*, 38, 29–36.

Wagenet, R.J., Biggar, J.W. & Nielsen, D.R., 1977 — Tracing of transformations of urea fertilizer during leaching. *Soil Science Society of America Journal*, 41, 896–902.

Weber, J.B., Weed, S.B. & Ward, T.M., 1969 — Adsorption of s-triazines by soil organic matter. *Weed Science*, 17, 417–421.

Weber, J.B., 1972 — Interactions of organic pesticides with particulate matter in aquatic and soil systems. *In* Gould, R.F. (editor), Fate of Organic Pesticides in Aquatic Environment. *American Chemical Society,* 111, 55–120.

Weber, J.B. & Weed, S.B., 1968 — Adsorption-desorption of diquat, paraquat and prometone in montmorillonitic and kaolinitic clay minerals. *Soil Science Society of America Proceedings*, 32, 485–487.

Weed, S.B. & Weber, J.B., 1974 — Pesticide — Organic matter interactions. *In* Guenzi, W.D. (editor), Pesticides in Soil and Water. *Soil Science Society of America Inc. Publisher, Madison, Wisc. USA*, 39–66.

Yaron, B., Gerstl, Z. & Spencer, W.F., 1985 — Behaviour of herbicides in irrigated soils. *Advances in Soil Science*, 3, 121–211.

Appendix 1

Workshop report

This workshop, on the evaluation of the groundwater pollution potential of pesticides was one of three conducted at the *Aquifers at Risk Conference*. These workshops were based on a research project entitled *Groundwater Quality: A systematic basis for aquifer protection in rural areas* funded by the Land and Water Resources Research and Development Corporation of Australia. The presently considered workshop examined the factors controlling and methods for modelling the mobility and persistence of pesticides within the soil profile with respect to their potential for groundwater pollution. The other two workshops, dealing with spatial modelling for aquifer vulnerability and design methods for sustainable land-treatment of rural industry and sewage effluent, are reported elsewhere in this volume.

The objectives of this component of the project are: (1) to quantitatively define the extent to which commonly used pesticides present a hazard in terms of groundwater pollution as a result of their mobility through soil profiles; (2) in practice to provide a detailed understanding of the physical, chemical and biological processes involved in the leaching of different pesticides in Australian soil profiles; and (3) to identify appropriate parameters and develop a comprehensive model to enable the realistic description and prediction of potential pesticide movement to groundwater under different soil and climatic conditions.

The objectives of the workshop were to disseminate information on current progress in understanding the nature of the processes determining the mobility of pesticides and methodologies available for modelling their transport within soil profiles. Feedback was sought from workers in relevant organisations on the problems likely to be encountered in acquiring relevant data and in developing management models of practical use.

Workshop presentations

The workshop was chaired by Richard Lakey (Department of Conservation, Victoria).

Graham Aylmore (see paper above) outlined the current progress made in understanding the interactions of pesticide chemicals with soil constituents and the influence on these processes of soil properties, such as texture, clay mineral species, organic matter content, pH, salts and solvents present, with particular reference to Australian soils and conditions. While biological or chemical degradation and transformation of pesticides to their metabolites will determine the residence times of the parent compounds in the soil and will undoubtedly affect the extent to which they pose a pollution hazard, the significance of these processes in soils under Australian conditions is poorly understood. Similarly, the significance of other factors, such as sorption-time dependency arising both from structural limitations on diffusion into micropores as well as from the kinetics of the sorption process itself, and the effects of competition between differing chemicals for sorption sites in any particular situation, need to be assessed.

Rai Kookana (see paper above) summarized the multiplicity of predictive models ranging from process-based models employing the classical convection–diffusion–dispersion equations to stochastic models, the latter incorporating a random component and producing results in terms of probability distributions. While comprehensive process-based research models provide quantitative estimation of pesticide behaviour in soils, these are invariably "data-hungry" and likely to be too cumbersome for use in field situations. Management models put relatively less input data demand on the system and are capable of predicting pesticide behaviour in the field. However, few of these have actually been tested in the field. On the other hand, simple screening models designed to compare the relative mobility of pesticide chemicals, require few input parameters and hence are very attractive. However, these are not suitable for accurately predicting the environmental fate of a given pesticide.

Ian Ferris (this issue) dealt with the practical implications of these considerations in relation to the new generation of relatively water-soluble sulfonylurea herbicides. He illustrated and emphasised the enormous benefit of pesticide use to Australian farmers in sustaining the viability of our farming system in difficult economic times. He cited risk assessment case studies which illustrated the dependency of leaching potential on the chemistry of the soil environment. While in one particular case, in a typical Western

Australian sandy soil, there was not a great deal of leaching, the results were qualified by the sodicity and alkalinity of the soil and exhibited substantial variation. In other cases, in Victoria and South Australia there was evidence that long-term applications can result in accumulation and in some circumstances substantial leaching occurred. Coupled with overseas data the conclusion is that sulfonylureas are very vulnerable to leaching and clearly do leach. A major factor influencing leaching was rainfall infiltration and recharge.

Overview

Graham Aylmore briefly summarized the major points of concern arising from the previous presentations. He stressed the importance of recognizing the rooting and unsaturated zone as having a major influence in filtering out contaminants and in determining the extent to which pesticides will move from the surface down to the groundwater. The data presented clearly illustrated the dependence of pesticide mobility on the nature and chemistry of the pesticides and the way they are influenced by the chemical environment of the soil. The different modelling approaches serve different purposes with simple screening models giving useful comparisions of the likely impact of the hazards posed by these materials and research models being essentially of use to demonstrate mechanisms; for example time dependency of sorption processes. Particular emphasis was placed on the need to define the degree of complexity with which fundamental processes need to be treated in effective management models and the extent of characterisation of the variety of physical, chemical and biological parameters required to avoid problems of site specificity.

Main points of discussion

Greg Davis (CSIRO Division of Water Resources, W.A.):

You have outlined a lot of things, which could take 50 years of study. What are your immediate aims in terms of the LWRRDC project? What is your strategy and what areas do hope to target?

Graham Aylmore:

Essentially we have two objectives. The first is to try to characterise the significance of the various factors involved and we have restricted ourselves to different representative classes of pesticide to try to get a handle on this. Initially we were working with laboratory-based experiments using soil columns and research-type models to evaluate the significance of the various mechanisms. We have also undertaken some field experiments at the Western Australian Horticultural Research Station at Medina, where we have applied representative pesticides in the field and monitored them over time by soil sampling and also by taking groundwater samples. The purpose of these studies is to determine how effectively existing screening and management models describe the processes that we are looking at and at the same time to refine these by investigating the processes in the laboratory. The overhead illustrates what I have been saying about the main points of concern and we are seeking feedback on these points. This emphasises firstly the importance of the unsaturated plant rooting zone. Secondly, there is the characterisation of sites: the sorptive properties, pH, and physical factors such as the soil structure, water repellency, and preferential flow paths. Thirdly, there is

the spatial varibility, and finally the number of pesticide classes.

Chairman:

The reality is that in many instances the number of residual pesticides, fungicides, and the like, are added simultaneously. It is not just a case of adding one continually to a particular paddock — you might apply two or three in the course of a normal agricultural cycle, and often these are applied together. What complexity does that pose for the research models in understanding the sorption process? Are the pesticides compatible and do they mix? I might add that working out what pesticides can be used together is a major headache for the farmer. The real question is what happens sub-surface. This is a very big issue.

Rai Kookana:

One area in which the mixing of a number of herbicides and pesticides together makes the situation complex is in the degradation process. It is not just the mixing of a number of herbicides; it is in fact that this induces a certain type of bacterial population which is capable of degrading one type rather than another. With repeated applications of the pesticide, if you apply 24D in a soil this year, next year, the year after, the degradation will be faster. It is in terms of degradation that the influence will be greatest.

Chairman:

So we could be looking at a collectively longer half-life?

Rai Kookana:

That could be so.

Graham Aylmore:

Competitive adsorption is a major complexing factor which needs to be understood and anticipated.

Libbie Lau (Lau and Associates, ACT):

With pesticides you can regard the fraction that is leached into groundwater as virtually a waste. But it is not as simple as that with pesticides. I gather you can not just cut back the amount of pesticide you apply. Can you change the application rate of the pesticide? Is that immutable, or can it be changed to stop the amount of leaching into the groundwater so that you apply only as much as you need.

Ian Ferris:

There are guidelines for the concentration of pesticides in groundwater. We have a standard. Normally, I have grave reservations about standards, but in this case I believe that the 100 parts per trillion standard for sulfonylureas is about the toxicological level where we see an effect on plants. I hasten to add that this does not apply to people. This does not pose a problem for human beings. The LD50s for all these compounds are greater than 5000 mg per kilogram, so they are not a toxicological threat to people, but they can be for plants and trees in particular. We have a toxicological level that has been formulated, and that is the one we should try to work to. We are now undertaking a fairly intensive program to try to look at the management package, and that includes reducing the rate and the frequency. In the case of

sulfonylureas in alkaline soils, a reduction in both the rate and the frequency will have to be achieved. By and large, the regulation of these compounds is fairly strict and we need to ensure that the existing regulations regarding these compounds are adhered to.

There is a problem. When these materials were first introduced, the companies established very long recropping periods for these compounds — about two to three years — and in most cases growers found that they could recrop the following year. Thus, the guidelines were ignored because farmers felt that they were not relevant. Quite clearly in some cases they are relevant. So perhaps we should reenforce the existing guidelines on these compounds, in particular in the high-risk areas. In the northern areas where the risk is not so great, maybe we should cut it down. We could probably increase the frequency in many instances. Long-term simulations have shown that there is no need to have such a low frequency of application.

I might add that these chemistries are applying very low use rates, and that is very important in terms of how we perceive this type of exercise. Many people argue that these chemicals are the bridge between our non-sustainable systems of agriculture, which utilise large quantities of fossil fuel and sustainable systems and substitute very low use rates of these materials for mechanical cultivation.

John Bauld (AGSO, ACT):

I am interested in the way that these models may or may not deal with degradation products. As I understand it, they approach the disappearance of the present compound that is applied to the system. In some cases, degradation products may behave differently in soils or in the water table, and they may have greater or lesser degrees of toxicity. I am not suggesting that this is true in all cases, but some of those may be just as important as the parent compounds.

Rai Kookana:

This is a very important point. We know that certain compounds have given a lot of problems to citrus growers in Florida because they oxidise, first to sulfoxide and then to sulfones, which are equally toxic. One of our models, ERZM, has the capacity to deal with such problems. It has the capacity to include those daughter compounds which, as you said, are in some cases even more toxic.

One example of this is fenamiphos, a nematicide used in horticulture. This is incorporated in the soil as sulfoxide and sulfone. Because of the polarity of these daughter compounds, they are more mobile but more toxic. Therefore, it is very important to consider those daughter compounds.

Graham Aylmore:

We have done some work on materials that degrade into metabolites and we are trying to incorporate that into the management models.

Chairman:

What happens when sulfonylureas leach through to the water tables? What work has been done on that?

Ian Ferris:

Sulfonylureas derive in part from sulfonomide, which has been widely used since the 1930s as a bacterial static agent. Another part is triazine — most of us are familiar with atrazine and simazine, for example — and there is a bridge component as well. The unique feature is that when you put these chemistries together the result is an extremely active compound, and this is a novel feature of sulfonylureas.

The high activity is great for sustainability because it requires less energy. We do not have to put as much out and it is environmentally friendly for a lot of non-target organisms. Those are the good features.

The bad feature for analytical chemists is that we cannot measure them because at toxicological concentrations for highly susceptible plants, we do not have any adequate analytical procedures. The closest we have at the moment are the Eliza techniques, which although available, can be very unreliable. I would not recommend them. To get down to that 100 parts per trillion level — and I think you will all appreciate that it is a low level — is really a tough job which will require a lot more work.

Peter McDowall (Commonwealth Environmental Protection Agency, ACT):

There are indicated plant techniques using a root involving the use of lentil bioassays and things like that, using a specific known variety of lentil grown in soils. By measuring the root growth of that lentil you can quickly estimate the amount of chemistry left in the soil.

Ian Ferris:

We use lentil bioassays for nearly all our analytical work and our validation. There are two problems. The technique is very time-consuming, and its reliability is very questionable unless you have a lot of experience with it. In general, the technique works, but it is subject to a lot of interactions. For example, in these highly sodic soils (up to pH 10) the lentils will not grow, or they are severely affected. There are big interactions and it is a bit of a problem.

Graham Aylmore:

I would like to ask some of the hydrologists to comment on our emphasis on the rooting zone and unsaturated zone as the major filtration region for pesticides. My observation is that very often hydrologists tend to think of soils as a black box: "some goes in, some comes out, some stays in" and that the system can be readily characterised in a simple way. Am I right or am I wrong in thinking that?

Chris Barber (CSIRO Division of Water Resources, WA):

I particularly like the risk approach that you use to assess the leaching potential. But it struck me at the time that it only told half the story; the rest of it was, where did it go once it got through the rooting zone? That highlights the link with the vulnerability assessment project which really focuses on the groundwater resources. It is important to link the two and not just keep them separate. You will need to have a broader regional idea of what happens in the groundwater resource, as well as the localised information.

George Gates (Department of Water Resources, NSW):

We have recently been looking at pesticides and herbicides in groundwater in the cotton-growing areas of New South Wales. I guess we have sampled fewer than 100 bores, but we have found atrizine in about six out of 100 at depths in the water table of perhaps 25 m from the surface. The level has been between one and four parts per billion. Does it surprise you to find atrizine at that depth? Does it cause you concern?

Ian Ferris:

Chris Barber raised a good point. I did not mean to imply that there is no problem from sulfonylureas. Obviously they impinge on farmers whose recropping is affected. If that involves a contained, perched water table, we do have a potential problem. Obviously we are working very hard to try to address that specific question. I try to refer to my risk analysis in terms of the whole of Australia. It is a national picture, but local people can be very badly affected, so we need to work on some of those site-specific issues.

On the question of atrizine, I must say that I am not really surprised about the problem that George raised in the cotton-growing areas. Although our models suggest that movement through the soil structure will not cause a large leaching problem, we certainly can have preferential flow in some of these areas. We have the possibility of preferential flow and we also have the possibility of movement of soils down the profile.

In case people are not familiar with this area of discussion, I point out that these soils are sodic, very often they can disperse under the influence of rainfall, and some of that soil can actually move down the profile, taking some of these materials, such as atrizine, which normally would not leach. They can get down to more than a metre below the rooting zone, so some of these hydrological processes can be important. In some cases, we have shallow water tables, and in other cases we have what I regard as unsafe disposal practices for atrizine. Perhaps I should broaden that out a little. Although it is registered for such use, I would not really recommend using atrizine in irrigation water situations. You can imagine what it is used for: weed control on river banks and aquatic weed control, where the risk is greater.

We must also couple that with point source pollution, i.e. the way people handled disposal of containers in the past. These were not little containers, like those used for sulfonylureas, but huge drums. In the past, those drums were not recycled, but dumped in the local municipal tips. We have a number of potential sources which I would not regard as non-point source pollution. I have a feeling that if we look hard enough we will find a point source, or with aquatic weed control almost a point source application.

Pere Wyles (Sydney Water Board):

I am curious as to how your models might handle a situation such as that described earlier: the one at Yass, where there is highly volatile chemistry as a result of clearing the surface. Would your models not give unpredictable results, or are they all right?

Rai Kookana:

I thought we had already demonstrated so much more complexity in that instance. I think we are already too far away from the real situation because there are so many aspects which we do not understand too well. I do not quite know what to say about this one.

Graham Aylmore:

I think the answer is that you cannot be all things to all men. You can just try to solve the problems one at a time as best you can. There is just such complexity in the whole system. We have to learn to crawl before we can walk. We do not pretend that we can rapidly handle every situation.

Ray Evans (AGSO, ACT):

Are there any strategies in train to identify on a rigorous basis the areas in which we might expect to find potential problems? That might be of some use in helping to target research results towards problems in the community.

Graham Aylmore:

We are certainly seeking input from people nationally on the identification of problems. However, we have not yet reached the point where we want to go out and be troubleshooters, tackling specific field problems that people might come up with. I do not see us as having that state-of-the art expertise. Anyone who is doing any pesticide work anywhere gets inundated by investigative journalists, who know of a particular problem and want to involve you in solving it. As I said, I do not see us as troubleshooting, but we are interested in receiving information or input from people.

Ray Evans:

My impression is that much of the investigation is occurring on an opportunistic basis, where problems are being identified in the environment. Is there any plan to collect pesticide-use data on a national scale?

Graham Aylmore:

We would certainly like to, and intend to do that. We only started this program in the last six months. But certainly we would have that approach in mind further down the track.