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SID 5 Research Project Final Report

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Executive Summary

7. The executive summary must not exceed 2 sides in total of A4 and should be understandable to the intelligent non-scientist. It should cover the main objectives, methods and findings of the research, together with any other significant events and options for new work.

Sorption of a pesticide to soil constituents determines its availability to non-target organisms and its potential to move to groundwater or surface waters. Pesticide fate modelling at the first tier of regulatory environmental risk assessments assumes that pesticide sorption is instantaneous and fully reversible. This implies that sorption coefficients are constant over time. However, sorption has frequently been observed to increase with increasing time of interaction with the soil. This is referred to as aged sorption.

Experimental studies that demonstrate an increase in pesticide sorption with time are increasingly submitted to regulatory authorities as part of the regulatory data package. The results of these studies are used by applicants to revise estimates of predicted environmental concentrations in groundwater. Pesticide leaching models that simulate changes in sorption with time are used for this purpose.

There is currently a lack of agreed and clear guidance on how aged sorption studies should be conducted and interpreted and how the results should be implemented in regulatory exposure assessments. The aim of the current project was to address this issue. The work was jointly undertaken by The Food and Environment Research Agency in the UK and Alterra in the Netherlands. The specific objectives were:

1. To review model concepts and experimental techniques to characterise time-dependent sorption;
2. To measure time-dependent sorption in laboratory studies for a range of soils and pesticides using various experimental techniques;
3. To derive model input parameters from the experimental data and evaluate the effect of the experimental methodology, data handling and parameter estimation techniques on the results;
4. To develop and disseminate guidance on how aged sorption studies should be conducted, analysed and used in regulatory assessments.

Existing experimental methodologies to measure aged sorption were reviewed. The aim was to define the method that would be most suitable for use within the risk assessment for pesticides in the environment. The method must be reliable and reproducible, give realistic parameters for the field situation but also be relatively simple with limited effort. The most promising method was a laboratory incubation study. Variations of the experimental design for this type of study were tested experimentally.

A review of approaches to describe aged sorption mathematically was undertaken. A two-site model was considered to be the best option for use in the regulatory context. This model is implemented in the

pesticide leaching model PEARL. A sensitivity analysis with PEARL demonstrated that the results of leaching assessments are very sensitive for changes in the parameters of the two-site aged sorption model. It is thus important that the parameters are reliable. The derivation of aged sorption parameters was tested within this project for a large range of hypothetical datasets. Criteria for the acceptability of model parameters were identified based on the results.

A comprehensive guidance document was drafted based on the findings of the research for this project. The document gives recommendations on the experimental protocol for aged sorption studies, on the fitting of the two-site model against the data from these studies and it describes on how the results should be implemented in regulatory exposure assessments. The guidance was developed for use in the UK with the intention to stimulate discussion on this topic at the European level, thereby facilitating the harmonisation of guidance across Europe. The draft guidance was discussed at a workshop with representatives of European regulatory authorities, academia, consultancies and industry. The feedback included comments on the experimental protocol and data handling procedures. The participants raised concerns over the acceptance criteria for the model parameters and the guidance on the implementation of aged sorption into regulatory leaching assessments. There was a general agreement that the guidance should be tested against real datasets. The participants expressed a wish for additional guidance on aged sorption of metabolites and on the use of field studies. There was consensus that a harmonised guidance document should be developed at the European level and the mechanisms for this were discussed.

A workshop report will be published on the CRD website. The report will provide details of all the documents that were discussed at the workshop along with summaries of the comments from the workshop participants. The testing of the proposed guidance against real datasets has been initiated by ECPA. The guidance will be revised by CRD based on the results from the testing phase and the comments received at the workshop. The modified version of the draft guidance document will then be forwarded to EFSA for further development at the European level.

Project Report to Defra

8. As a guide this report should be no longer than 20 sides of A4. This report is to provide Defra with details of the outputs of the research project for internal purposes; to meet the terms of the contract; and to allow Defra to publish details of the outputs to meet Environmental Information Regulation or Freedom of Information obligations. This short report to Defra does not preclude contractors from also seeking to publish a full, formal scientific report/paper in an appropriate scientific or other journal/publication. Indeed, Defra actively encourages such publications as part of the contract terms. The report to Defra should include:
- the scientific objectives as set out in the contract;
 - the extent to which the objectives set out in the contract have been met;
 - details of methods used and the results obtained, including statistical analysis (if appropriate);
 - a discussion of the results and their reliability;
 - the main implications of the findings;
 - possible future work; and
 - any action resulting from the research (e.g. IP, Knowledge Transfer).

Introduction

Experimental laboratory studies that demonstrate an increase in pesticide sorption with time are increasingly submitted to the Chemicals Regulations Directorate as part of the regulatory data package. The results of these studies are used by applicants to revise estimates of predicted environmental concentrations in groundwater. There is currently a lack of agreed and clear guidance on how aged sorption studies should be conducted, interpreted and hence used in regulatory exposure assessments. The proposed project developed guidance on the experimental design and data analysis of time-dependent sorption studies for use in regulatory exposure modelling. The specific objectives were:

1. To review model concepts and experimental techniques to characterise time-dependent sorption;
2. To measure time-dependent sorption in laboratory studies for a range of soils and pesticides using various experimental techniques;
3. To derive model input parameters from the experimental data and evaluate the effect of the experimental methodology, data handling and parameter estimation techniques on the results;
4. To assess whether time-dependent sorption parameters derived in laboratory studies are suitable to describe pesticide behaviour in undisturbed lysimeters;
5. To develop and disseminate guidance on how aged sorption studies should be conducted, analysed and used in regulatory assessments.

A detailed research report and a guidance document have been generated within this project. These will be made available in full on the CRD website. Only a brief summary of the work undertaken is given below.

Summary of research

Several experimental methods to measure aged sorption of pesticides in soil were reviewed and tested experimentally. This aimed at identifying the method that would be most suitable for use within the risk assessment for pesticides in the environment. The method must be reliable and reproducible, give realistic parameters for the field situation, but it must also be relatively simple and limit the experimental effort.

The most promising method was a laboratory study where soil samples are incubated with pesticide for different time intervals. The advantages of measuring sorption during an incubation study are:

- The moisture content of the soil during incubation is realistic in contrast to the small soil:solution ratios in studies with soil suspensions;
- The experimental conditions are controlled: the moisture content of the soil and temperature are kept constant during the experiments; soil samples can be mixed to ensure even distribution of pesticides through the soil, and the parameters necessary to describe the experimental conditions can be independently measured.

Other methods that are used to measure the increase of sorption with time are batch sorption studies where adsorption and desorption are measured in soil suspensions, column experiments and field experiments. The experimental conditions during column or field experiments may be more realistic for the field situation than incubation under laboratory conditions. However, the experimental effort is much larger than for laboratory studies, the conditions are more heterogeneous and the methods are less suitable to be standardised.

Several variations of the methods for incubation studies in the laboratory were tested. Soil samples were treated with pesticides and incubated at a constant moisture content and temperature for different time intervals. After incubation, the amount of sorption was determined by measuring the pesticide concentration in solution, either by using the centrifugation method or by aqueous extraction for 1 hour or 24 hours.

The 24-h aqueous extraction method was found to be the most suitable for deriving the aged sorption parameters in the context of pesticide risk assessment. The method fits the requirements for a relatively simple and reproducible method. Moreover, the method is consistent with the current operational definition of equilibrium sorption used in pesticide risk assessments, which is based on the amount of sorption in a soil suspension shaken typically for 24 hours (OECD guideline 106). The increase in sorption determined with the 24-h aqueous extraction method reflects the increase in sorption beyond the usual 24-h equilibrium sorption.

The incubation of soil aggregates gave results equal to those from the incubation of sieved soil. The method with the least effort (sieved soil) was recommended.

Various modelling approaches that describe aged sorption mathematically were reviewed. The two-site model was considered to be the best option for use in regulatory leaching models. The model describes equilibrium sorption, non-equilibrium sorption and degradation with a total of 6 parameters. Other models use the same number or more parameters. The two site model is the most common mathematical description of time-dependent

sorption that is currently used in the regulatory context. It is integrated into the most recent FOCUS versions of the pesticide leaching models PEARL, MACRO, PELMO and PRZM.

A sensitivity analysis with PEARL demonstrated that the results of leaching assessments are very sensitive for changes in aged sorption parameters. It is thus important that the parameters are reliable. The derivation of aged sorption parameters was tested for a large range of hypothetical datasets. It was not always possible to derive the true parameter by model fitting. For some parameters combinations, the model calculations are not sensitive enough for the parameters or the correlation between parameters hinders the accurate derivation of the true values. It was shown that the confidence interval of the derived parameters can be used to evaluate their reliability.

The results from the research for this project are reported in detail within the research report (DEFRA, 2010a).

Guidance document

A comprehensive guidance document was drafted based on the findings of the research for this project. An experimental protocol details how aged sorption laboratory incubation studies should be conducted. It is recommended to integrate aged sorption measurements into standard regulatory sorption and degradation studies following OECD guidelines. The guidance document outlines quality criteria and data requirements for aged sorption studies. These must be met before an aged sorption model can be fitted to the data. Guidance is given on the procedures and tools for parameter optimisation. It is described how the goodness of fit of the aged sorption model and the acceptability of the parameters should be assessed. The final section of the guidance document gives recommendations on how to integrate aged sorption into the regulatory exposure assessment. Brief comments are made on aged sorption studies for metabolites.

The full draft guidance document (DEFRA, 2010b) will be made available on the CRD website.

Workshop

The proposed guidance document and underpinning research were presented to European stakeholders at a workshop in April 2010. The purpose of this meeting was to collate feedback on the guidance from representatives of European regulatory authorities, academia, consultancies and industry. The participants were assigned to breakout groups who were asked to discuss four questions related to the technical details of the guidance and the regulatory implications:

1. Do the participants agree with the technical guidance?
2. How can the procedures for deriving time-dependent sorption parameters be incorporated into the standard suite of regulatory studies?
3. How should higher and lower tiers of the risk assessment be integrated?
4. How should the guidance be taken forward after the workshop?

Detailed notes were taken in each of the breakout groups. The groups reported their main conclusions back to the plenum. The participants felt that guidance on aged sorption is needed and they welcomed CRD's initiative to develop draft recommendations. All breakout groups appreciated the opportunity to provide feedback. There were comments on some details of the experimental protocol and data handling procedures. The participants raised concerns over the acceptance criteria for the parameters and the guidance on the implementation of aged sorption into regulatory leaching assessments. There was a general agreement that the guidance should be tested against real datasets. The participants expressed a wish for additional guidance on aged sorption of metabolites and on the use of field studies. There was consensus that a harmonised guidance document should be developed at the European level and the mechanisms for this were discussed.

A workshop report will be published on the CRD website. The report will provide details of all the documents that were discussed at the workshop along with summaries of the comments from the workshop participants.

Future work

The current project developed guidance on aged sorption studies for use in the UK with the intention to stimulate discussion on this topic at the European level, thereby facilitating the harmonisation of guidance across Europe. This initiative was well received by all stakeholders present at the workshop. It was agreed that the next phase of the guidance development should include its testing against additional real data from aged sorption laboratory studies. The European Crop Protection Association (ECPA) will provide datasets and fund the evaluation of these data based on the current version of the guidance. This will be carried out by an independent expert. CRD will be consulted during this process. The guidance will be revised at the UK level based on the results from the testing phase and the comments received at the workshop. The modified version of the draft guidance will then be forwarded to EFSA for further development at the European level.

References to published material

9. This section should be used to record links (hypertext links where possible) or references to other published material generated by, or relating to this project.

DEFRA (2010a). Development of guidance on the implementation of aged soil sorption studies into regulatory exposure assessments. Research report for DEFRA project PS2235. The Food and Environment Research Agency and Alterra.

DEFRA (2010b). Proposed guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments. The Food and Environment Research Agency and Alterra.

A report from the workshop held in April 2010 including the comments received from the participants will be placed on the CRD website. All PowerPoint presentations given at the workshop, the questions discussed in the breakout groups and the research report and guidance document referred to above will also be made available via the website.