ALTERRA
WAGENINGEN**UR**

Methods for estimating the vapour pressure of organic chemicals

Application to five pesticides

M. Leistra

Methods for estimating the vapour
pressure of organic chemicals

Methods for estimating the vapour pressure of organic chemicals

Application to five pesticides

M. Leistra

Alterra report 2215

Alterra, part of Wageningen UR
Wageningen, 2011

Abstract

Leistra, M., 2011. *Methods for estimating the vapour pressure of organic chemicals;* Application to five pesticides. Wageningen, Alterra, Alterrareport 2215. 60 pp.; 2 fig.; 25 tab.; 102 ref.

When studying and modelling the volatilisation of pesticides from crops, their vapour pressure is an essential property. In the critical evaluation of vapour pressures stated by various sources, problems were encountered. Therefore, an inventory was made of readily-usable methods for estimating vapour pressures of organic chemicals, for checking the stated values. When applied to some of the five example pesticides, the estimates were at the same level as the stated values. However, for other pesticides there were substantial differences. Unfortunately, there is a wide range of uncertainty in both measurement and estimation of comparatively low vapour pressures. The solid (crystalline) and sub-cooled-liquid states of the chemical have to be distinguished when specifying and using vapour pressures, because the latter can be much higher. The influence of the uncertainty in vapour pressure on the source strength of volatilisation from plants is illustrated in a few computations. Only data for pesticides with accurately known vapour pressure are usable in the development and testing of computation models on the volatilisation from crops.

Keywords: air emission, boiling point, crop, estimation, fungicide, insecticide, model, plants, chlorothalonil, chlorpyrifos, lindane, pirimicarb, quinoxyfen, registration, volatilisation.

The pdf file is free of charge and can be downloaded via the website www.alterra.wur.nl (go to Alterra reports). Alterra does not deliver printed versions of the Alterra reports. Printed versions can be ordered via the external distributor. For ordering have a look at www.rapportbestellen.nl.

Alterra report 2215
Wageningen, September 2011

Contents

Preface

In the framework of the registration procedure for pesticides (EU, supplemented by member states), estimates are needed on the source strength and extent of volatilisation from the crops after spraying. For that purpose a computation module was developed that has been incorporated in the comprehensive PEARL model for pesticide behaviour in soil-plant systems. The vapour pressure of a pesticide is an essential input datum for a model simulating volatilisation.

In the critical evaluation of statements on the vapour pressure of pesticides, serious problems were encountered. This makes it necessary that methods are available for estimating the vapour pressure. Such methods can be used in checking the reliability of stated values.

This study gives a survey of readily-usable methods for estimating the vapour pressures usually based on molecular structure in combination with other physico-chemical properties. Where possible, the methods are applied to five example pesticides whose properties are used in the development and testing of volatilisation models. The impact of the uncertainty in vapour pressure on the estimation of the source strength of volatilisation from plants is illustrated in a few computations with the PEARL model.

Samenvatting

De dampdruk van een bestrijdingsmiddel is de belangrijkste eigenschap bij de vervluchtiging vanaf gewassen. Empirische methoden voor het schatten van de vervluchtiging vanaf gewassen maken vooral gebruik van de dampdruk. Rekenmodellen zijn ontwikkeld voor het schatten/voorspellen van de vervluchtiging (gewas, bodem, water) en de dampdruk is een essentieel invoergegeven voor zulke modellen.

Bij het gebruik van dampdrukken in berekeningen kan men op problemen stuiten. In een deel van de gevallen kan de herkomst van een bepaalde (oudere) waarde (bijv. in een handboek) niet worden achterhaald. Voor nieuwere middelen kan de methode voor het bepalen van de dampdruk in een vertrouwelijk rapport beschreven zijn (kwaliteit niet te controleren), alleen het eindresultaat is dan openbaar. Men kan stuiten op onlogische verschillen in de dampdruk van structuur-verwante verbindingen. Zelfs komt het voor dat er sterk verschillende waarden voor de dampdruk van een bestrijdingsmiddel worden vermeld. Indien de gemeten vervluchtiging van een bestrijdingsmiddel sterk afwijkt van berekening (met een getoetst model) op basis van de opgegeven dampdruk, dan rijst de vraag hoe betrouwbaar die dampdruk is.

De bepaling van de dampdruk van een bestrijdingsmiddel kan lastig zijn, bijvoorbeeld omdat het niveau lager is dan dat bij veel industriële chemicaliën. De meeste bepalingsmethoden hebben een beperkt traject van waarden (veelal relatief hoog) dat nauwkeurig kan worden gemeten.

In de laatste decennia zijn schattingsmethoden voor de dampdruk ontwikkeld, veelal gebaseerd op molecuulstructuur in combinatie met fysisch-chemische eigenschappen. Ook schattingsmethoden hebben een beperkt bereik van te schatten waarden (d.i. het traject waarvoor ze getoetst zijn) en ze kunnen alleen gelden voor specifieke groepen van verbindingen.

Deze studie geeft een overzicht van methoden voor het schatten van de dampdruk van bestrijdingsmiddelen. Omdat het kookpunt (niet altijd beschikbaar) in diverse schattingsmethoden wordt gebruikt, worden eerst methoden voor het schatten van het kookpunt besproken. De inventarisatie is vooral gericht op handzame berekeningsmethoden, die geen sterk-gespecialiseerde kennis vereisen. Daarnaast zijn er sterk gespecialiseerde methoden, die vaak zijn geprogrammeerd voor berekeningen met computers. Een voorbeeld van het gebruik van een geprogrammeerde methode wordt gegeven.

Voor zover mogelijk worden de methoden toegepast bij de schatting van de dampdruk van vijf bestrijdingsmiddelen: chloorthalonil, chloorpyrifos, lindaan, pirimicarb en quinoxyfen. De status van de eerder vermelde dampdrukken (literatuur, eindpuntenlijst registraties, databestanden) van elk van de verbindingen wordt beschreven. De dampdrukken geschat voor een bestrijdingsmiddel worden vergeleken met de eerder vermelde waarden, in een poging om de meest waarschijnlijke waarde af te leiden voor invoer in berekeningen betreffende de vervluchtiging.

Een aanzienlijk aantal bestrijdingsmiddelen heeft een smeltpunt dat boven de omgevingstemperaturen ligt, zodat ze zich in vaste toestand kunnen bevinden (bijv. op een gewas). Het blijkt voor deze middelen essentieel twee toestanden te onderscheiden - de vaste (kristallijne) toestand en de onderkoelde-vloeistof toestand - omdat de dampdruk van laatstgenoemde bij een bepaalde temperatuur aanzienlijk hoger kan zijn. Allereerst is van belang voor welke toestand de metingen en schattingen zijn uitgevoerd. Vervolgens is het de vraag welke toestand het meest representatief is voor de beschrijving van verschillende processen, zoals vervluchtiging vanaf het gewas en verdeling over bodem, water en lucht.

Een versie van het PEARL-model voor het gedrag van bestrijdingsmiddelen in bodem-plant systemen werd gebruikt om berekeningen te maken voor de vervluchtiging van het fungicide quinoxyfen vanaf planten in een windtunnel. Daarbij werd gebruik gemaakt van resultaten van computer simulaties van de vervluchtiging van radioactief-gemerkt parathion-methyl in dezelfde studie (modeltoets).

De vermelde lage dampdruk van 0.012 mPa bij 293 K kan de vervluchtiging van 15% van de dosering van quinoxyfen vanaf planten niet verklaren. Dit lukt ook niet bij aanname van trage penetratie in de planten en langzame fototransformatie op het plantoppervlak. Daarentegen kan een hogere dampdruk van 0.10 mPa (bij 293 K) in het schattingstraject de mate van vervluchtiging van quinoxyfen wèl verklaren. Dit in combinatie met matig tot lage snelheden van de concurrerende processen, die aannemelijk zijn op basis van beperkte literatuurgegevens.

Samenvattend kan men stellen dat de betrouwbaarheid van een opgegeven dampdruk een serieus probleem kan zijn. In registratieprocedures moet een kritische beoordeling van de wijze van bepalen van de dampdruk plaatsvinden. Schattingsmethoden dienen optimaal te worden benut om een indruk te krijgen van de betrouwbaarheid van de opgegeven dampdrukken. Dit geldt het sterkst bij het niet openbaar zijn van de bepalingswijze, bij tegenstrijdige dampdrukken en bij vervluchtigingsgedrag dat niet overeen lijkt te komen met de opgegeven dampdruk. Het gebruik van de experimentele resultaten voor een bestrijdingsmiddel bij het ontwikkelen en toetsen van een rekenmodel voor vervluchtiging vereist een grote mate van zekerheid over de waarde van zijn dampdruk.

Summary

The vapour pressure of a pesticide is its most important property for the volatilisation from crops. Empirical methods for estimating volatilisation from crops utilise the vapour pressure as main parameter. Computation models have been developed for the estimation/prediction of volatilisation (from crops, soil, water) and vapour pressure is an essential input datum for such models.

When using vapour pressures in computations, problems can be met. In various cases, the origin of a certain (old) value (e.g. in a handbook) cannot be traced. For newer compounds, the method of determination of the vapour pressure may be described in a confidential report (quality cannot be checked); then only the final result is public information. Non-logical differences in the vapour pressure of structurally-related compounds may be encountered. In some cases even different values of the vapour pressure of a pesticide are reported. When the measured volatilisation behaviour of a pesticide deviates from computation (with a tested model) based on the stated vapour pressure, the question rises how reliable that vapour pressure is.

The determination of the vapour pressure of a pesticide may be cumbersome, e.g. because its level is lower than that of many industrial chemicals. Most determination methods have a limited range of values (often comparatively high) that can be measured accurately.

In recent decades estimation methods for the vapour pressure have been developed, which are usually based on molecular structure in combination with physico-chemical properties. Estimation methods also have a limited range of values to be estimated (i.e. the range for which they have been tested) and they may only apply to specific groups of compounds.

This study gives a survey of methods for the estimation of the vapour pressure of pesticides. Because the boiling point (not always available) is used in various estimation methods, first of all methods for estimating boiling points are discussed. This inventory is mainly aimed at easily-applicable calculation methods, which do not require highly specialised knowledge. Besides, there are highly-specialised methods, often programmed for calculations with computers. An example of the use of a programmed method is given.

As far as possible, the methods are applied in the estimation of the vapour pressure of five pesticides: chlorothalonil, chlorpyrifos, lindane, pirimicarb and quinoxyfen. The status of the vapour pressures given earlier for each pesticide (literature, list of endpoints in registrations, data bases) is described. The vapour pressures estimated for a pesticide are compared with the earlier stated values, in an attempt to derive the most probable value for input in computations on volatilisation.

A considerable number of pesticides has a melting temperature above the environmental temperatures, so they can be in solid state (e.g. on a crop). For these pesticides it is essential to distinguish two states - the solid (crystalline) state and the sub-cooled-liquid state - because the vapour pressure at a certain temperature can be distinctly higher for the latter. First of all it is important for which state the measurements and estimations were carried out. Subsequently the question is which state is most representative for the description of various processes, like volatilization from the crop and partitioning over soil/water/air.

A version of the PEARL model for the behaviour of pesticides in soil-plant systems was used to make computations on the volatilisation of the fungicide quinoxyfen from plants in a wind tunnel. In doing so, the

results of computer simulations on the volatilisation of radiolabelled parathion-methyl in the same study were used (model test).

The stated low vapour pressure of 0.012 mPa at 293 K cannot explain the volatilisation of 15% of the dosage of quinoxyfen from the plants. Neither can this volatilisation be explained assuming slow penetration into the plants and a low rate of phototransformation on the plant surfaces. Contrary to this, a higher vapour pressure of 0.10 mPa (at 293 K) in the estimation range can explain the extent of volatilisation of quinoxyfen. This in combination with moderate to low rates of the competing processes, which are plausible on the basis of limited literature data.

In summary it can be stated that the reliability of a stated vapour pressure can be a serious problem. In registration procedures the way of determination of a vapour pressure must be evaluated critically. Estimation methods have to be used as much as possible to get an impression of the reliability of the stated vapour pressure. This applies especially when the method of determination is not publicly available, when conflicting values are reported and when volatilisation behaviour does not appear to correspond to the stated vapour pressure. The use of the experimental results for a pesticide in the development and testing of a computation model for volatilisation requires a high degree of certainty on the value of its vapour pressure.

1   General introduction

The vapour pressure of a pesticide is an essential basic property in research on its volatility. In the rate of volatilisation from plants, vapour pressure is the single dominating characteristic of a pesticide (Smit et al., 1998). In the volatilisation of pesticides from soil and water, both its vapour pressure and its partitioning over the air, water and solid phases play an important part.

Measurement of low vapour pressures is complicated; various errors can easily be made. Examples of the main methods for measuring low vapour pressures (Mackay et al., 2006a) are:
1) Effusion methods, in which the pure substance in a container diffuses through a small hole into vacuum. The rate of mass loss or the torsion is measured.
2) The saturation method, in which the headspace above the pure substance is purged with inert gas. The concentration of the substance in the saturated gas stream is measured.
3) Comparison of the rate of volatilization with that of a reference compound with known vapour pressure.
4) Calculation from gas-chromatography retention times, compared with those of reference compounds with known vapour pressure.

Only in a limited number of cases, the way in which the vapour pressure of a pesticide was measured or estimated is fully documented in the published literature. More often, the method is described in a confidential report submitted in the framework of the registration procedure. Then, only the final result is available in the public List of Endpoints (e.g. EC-DGHC, 2010; NL-Ctgb, 2010) and in handbooks like that of Tomlin (2010). Without disclosed details it is not possible to evaluate the quality of the reported value of the vapour pressure and its uncertainties.

In some cases, even different values of the vapour pressure have been reported for a particular pesticide. For example, a wide range of values was published for the vapour pressure of chlorothalonil (Mackay et al., 2006b; Goel et al., 2007). In such cases the most probable value can possibly be selected on the basis of the detailed descriptions of the methods used for determination/estimation. If the source of a value is not known, it should be treated with suspicion (Baum, 1998). Estimation methods may be useful in the selection of the most probable value for the vapour pressure of a pesticide.

Recently, Joback (2009) described uncertainties in the data compilations of physical properties of organic compounds. The origin of the data may be obscure. It may be unknown whether the data were measured or estimated. Further, the data may have been extrapolated, e.g. from higher temperatures. The state of the compound (crystalline or sub-cooled liquid for vapour pressure) for which the value holds may be unspecified.

There may be a discrepancy between the measured volatilisation of a pesticide and the volatisation expected on the basis of the reported vapour pressure (without details on the method). This seems to be the case for the fungicide quinoxyfen, which showed distinct volatilisation (15% of the dosage) when sprayed on plants in a wind tunnel experiment (Wolters, 2003; Wolters et al., 2004). A very low vapour pressure of 0.012 mPa at 20 °C is included in the list of evaluation endpoints in registration procedures (EC-DGHC, 2003; NL-Ctgb 2005) and in a handbook (Tomlin, 2010). The uncertainty in the vapour pressures given in a handbook is illustrated by the remark of Tomlin (2003, page xvi): 'Where different values were supplied, the lowest figure has normally been chosen'. He did not give an argument for this approach.

Measurements of the vapour pressure are often preferred to estimates. However, the difficulties in measuring vapour pressure accurately should not be under-estimated. Especially when the values are low, the vapour pressure can fall below the range of accurate measurement by a method. Further, the requirements to the measurements are high: adequate amount of absolutely pure substance, no technical failures in the apparatus, highly selective measurement, etc. As the level of the vapour pressure becomes lower, the uncertainties in both measurements and estimations increase (Baum, 1998). As noted by Goel et al. (2007) vapour pressures for transformation products of pesticides are usually not available.

There is an urgent need of methods for estimation of the vapour pressure of pesticides and their transformation products in cases in which the available values are uncertain or missing. A literature study was set up to look for methods that can be used for such estimation. The estimation of vapour pressures is part of the more general activity of the research on QSPRs: Quantitative Structure-Property Relationships. Similar estimation procedures have been developed for properties like melting point, boiling point, solubility in water and octanol/water partitioning.

The normal boiling temperature (or boiling point; normal = at atmospheric pressure) of a pesticide gives a rough indication of the level of its vapour pressure at ambient temperatures and thus of its volatility. The higher this boiling point, the lower the expected vapour pressure. Various estimation methods for vapour pressure ask for the normal boiling point as one of the input data. For compounds like chlorpyrifos, pirimicarb and quinoxyfen, normal boiling point is not known. Therefore, this study starts with the estimation of the normal boiling point of pesticides (Chapter 3).

First of all, boiling point and vapour pressure of a compound are influenced by its molecular mass: heavier molecules tend to be less volatile. Volatility is counteracted by the intermolecular attraction forces between functional groups in the molecule. Examples of such forces are the Van de Waals-forces (non-polar groups), dipole-dipole attraction (polar groups) and hydrogen bonding (-OH, -NH groups, etc.). Besides, molecular symmetry and flexibility play a part in the level of the vapour pressure. They determine the density of the packing of the molecules in the liquid or solid state: the attractive forces between the molecules are much stronger at shorter   distances. Reviews on the molecular factors affecting boiling point and vapour pressure are given by Lyman (2000) and Dearden (2003).

This study deals with readily-usable estimation methods that can be used also by researchers not specialised in fundamental organic chemistry. The results are meant to be a guideline for estimation of the vapour pressure in future cases of uncertainty in the actual value for a pesticide. The more fundamental approaches (outside the scope of this study) require highly-specialised knowledge for the derivation of molecular descriptors of divergent types and they are usually programmed in a sofware package. Such methods can only be used by non-specialists via a user-friendly interface.

In this study, boiling point and vapour pressure are estimated for five pesticides for which well-defined volatilisation experiments have been published. These compounds and experiments seem to be useful in the testing and further development of a computation model for volatilisation from plants. The pesticides are: chlorothalonil, chlorpyrifos, lindane, pirimicarb and quinoxyfen. The estimated values (Chapter 5) are compared with data from the literature (where available) and from registration procedures (Chapter 4). Hopefully this allows the selection of the most probable value for the vapour pressure, as input for the computer simulations. For the many pesticides with the melting point above environmental temperatures it is essential to distinguish the vapour pressures of the solid (crystalline) and sub-cooled-liquid states, because the latter can be substantially higher at a certain temperature (Section 4.3; Section 5.8).

As an illustration of the problem of the uncertainty in vapour pressure, computations are carried out on the volatilisation of the fungicide quinoxyfen from plants in a wind tunnel (Chapter 6). Computations are carried out using a) the very low vapour pressure as cited from the company data in the EU list of endpoints (EC-DGHC, 2003) and b) a somewhat higher vapour pressure in the upper part of the range of values obtained by estimation methods in the present study.

2   Sources of physico-chemical properties of pesticides

There are various sources of physico-chemical properties of pesticides. Often these sources are evaluation dossiers in the framework of pesticide registration procedures. Such data are often derived from research reports submitted to registration authorities by the pesticide companies. Unfortunately, these reports are usually not publicly available, e.g. for research. This makes it impossible to evaluate the quality of the method of determination and thus the reliability of the results. Some compilations of pysico-chemical properties have been published in the literature or included in databases, but often their original source is not known and there was no quality check. The aim in this study is to use sources of information as closely as possible to the original reports. Besides publications on original research, the following sources were selected:

NL-Ctgb, 2010. Pesticides and active substances. Pesticides database. Board for the Authorisation of Plant Protection Products and Biocides. Wageningen, The Netherlands.
www.ctgb.nl

EC-DGHC, 2010. EU Pesticides database. Active substances. Review reports. Directorate General for Health and Consumers, European Commission, Brussels.
http://ec.europa.eu/food/plant/protection/evaluation/database_act_subs_en.htm

US-EPA, 2010. Peer Reviews of the US Environmental Protection Agency. Washington DC, USA.
www.epa.gov/pesticides

Tomlin, C.D.S. (ed.), 2010. The e-Pesticide Manual (15th ed.). A World Compendium. British Crop Protection Council. BCPC Publications Sales, Alton, Hampshire, UK.

Mackay, D., W.Y. Shiu, K.C. Ma and S.C. Lee, 2006b. Physical-chemical properties and environmental fate for organic chemicals (2nd ed.). Vol IV. Nitrogen and sulfur containing compounds and pesticides. CRC Taylor and Francis, Boca Raton Fl, USA.

UN-WHO, 2010. Environmental Health Criteria (EHCs) published by the UN World Health Organisation in the framework of the International Programme on Chemical Safety (IPCS), Geneva, Switzerland.
www.who.int/ipcs/publications/ehc/ehc_alphabetical/en/

SRC, 2010. Environment. Chemical fate and transport. Physical Properties Database (PhysProp). SRC, Syracuse NY, USA.
srcinc.com/what–we-do/environment.aspx

ChemSpider, 2010. Database of chemical structures and property predictions.
www.chemspider.com

In some cases, the procedure for determination of physico-chemical properties is described in the scientific literature. Attempts are made to collect all such original results on the vapour pressure of the example pesticides.

3   Estimating the boiling point

3.1   Introduction

Most estimation methods for the boiling point only use information on the chemical structure of the compound as input. Some methods also use the melting point. Various methods have been developed for specific homologous series of compounds (with closely related structures) (Horvath, 1992; Reinhard and Drefahl, 1999); these are often not applicable to a specific pesticide. Further, the estimation method should hold for the range of comparably high boiling points applicable to many pesticides. Most estimation methods for industrial applications deal with comparatively volatile compounds having low boiling points (Horvath, 1992; Reinhard and Drefahl, 1999). The emphasis in this report is on readily-usable calculation methods for the boiling point, that can be used by non-specialised researchers. In addition, there are advanced estimation methods on the basis of molecular descriptors, often programmed for the computer, used by more specialised researchers (Dearden, 2003).

In his review, Lyman (2000) recommended three hand-calculation methods for the boiling point: those of Yalkowsky et al. (1994), Simamora and Yalkowsky (1994) and Stein and Brown (1994). These methods and that of Simamora et al. (1993) are described briefly in this chapter and used to estimate the boiling point of the five example pesticides (if possible). Newer estimation methods are briefly discussed in the General discussion section (Section 3.8) and these should be considered also in future research.

An equation used in estimation methods for the boiling point is (Sanghvi and Yalkowsky, 2006):

$$T_b = \frac{\Delta H_v}{\Delta S_b}$$

(Eq. 1)

where: T_b = normal boiling point (K)

           ΔH_b = molar enthalpy of boiling (J mol^{-1})

           ΔS_b = molar entropy of boiling (J mol^{-1} K^{-1}).

This equation can be combined with Troutons rule: the molar entropy of boiling ΔS_b is roughly constant at 88 J mol^{-1} K^{-1} (e.g. Simamora and Yalkowsky, 1994). The rule holds for rigid organic molecules without hydrogen bonds.

A compilation of the reported melting points and boiling points of the five example pesticides is given in Table 3.1, together with an indication of their origin, if possible. Most of the selected references had access to the original reports (often confidential reports of companies). There is agreement on the value of the melting point of the pesticides, presumably because the values originate from the same (confidential) reports. Note that both 623 K and > 623 K were reported for the boiling point of chlorothalonil. The boiling point of chlorpyrifos could not be measured, because it decomposes below the boiling point. The two boiling points cited for lindane show some difference. Boiling points for pirimicarb and quinoxyfen were only reported by ChemSpider (2010); the origin of these values is not known. Table 3.1 illustrates the need of estimation methods for the (theoretical) boiling point, a quantity needed to estimate and check other physico-chemical properties (e.g. vapour pressure in Chapter 5).

Table 3.1

Reported melting points and boiling points of the example pesticides.

Pesticide	Melting point (K)	Boiling point (K)	Reference	Origin
Chlorothalonil	523	623	UN-WHO (1996)	Company reports
	525	> 623	NL-Ctgb (2001)	Draft EU Monograph
	525	> 623	EC-DGHC (2006a)	Company reports
	523	623	Mackay et al. (2006b)	Handbooks
	525	623	Tomlin (2010)	Not given
	523	624	ChemSpider (2010)	Not given
	523	623	SRC (2010)	Not given
Chlorpyrifos	315	Decomposes before boiling	NL-Ctgb (2009)	EU Monograph
	315	Decomposes before boiling	EC-DGHC (2005a)	Company reports
	315	-	US-EPA (2002)	Merck Index
	315	-	Mackay et al. (2006b)	Handbooks
	316	> 673	Tomlin (2010)	Not given
	315	433; decomposes	ChemSpider (2010)	Not given
	315	-	SRC (2010)	Not given
Lindane	386	561	UN-WHO (1991)	Company reports
	386	597	NL-RIVM (1992)	Company reports
	386	-	US-EPA (2001)	Company reports
	386	597	Mackay et al. (2006b)	Handbooks
	386	-	Tomlin (2010)	Not given
	386	561; 597	ChemSpider (2010)	Not given
	386	597	SRC (2010)	Not given
Pirimicarb	364	-	NL-RIVM (1989)	Company reports
	365	-	EC-DGHC (2006b)	Company reports
	364	-	Mackay et al. (2006b)	Handbooks
	365	-	Tomlin (2010)	Not given
	364	647	ChemSpider (2010)	Not given
	364	-	SRC (2010)	Not given
Quinoxyfen	380	-	NL-Ctgb (2005)	EU Monograph
	380	-	Tomlin (2010)	Not given
	380	696	ChemSpider (2010)	Not given
	380	-	SRC (2010)	Not given

The melting point of chlorpyrifos(-ethyl) is almost the same as that stated for chlorpyrifos-methyl (319 K; EC-DGHC, 2005b; Tomlin, 2010). Further, the boiling point of chlorpyrifos-methyl is given as > 633 K (EC-DGHC, 2005b).

3.2   Atom-count method of Yalkowsky et al. (1994)

In this method, the boiling point is calculated from the melting point and from characteristics of the chemical structure. The first equation proposed by Yalkowsky et al. (1994) to calculate the boiling point (their Eq. 19) reads:

$$T_b = 175 + 0.622\,T_m - 61.2\log(s) + 13.9N_1 \hspace{4cm} \text{(Eq. 2)}$$

where: T_b = normal boiling temperature (K)

T_m = melting temperature (K)

σ = external rotational symmetry number of the molecule (Appendix I)

N_1 = count of the number of atoms (larger than H and F) in the molecule.

This equation is relevant for chlorothalonil, lindane, pirimicarb and quinoxyfen, as their molecules only contain atoms that are assigned the value of 1 in the count.

A slightly different equation (their Eq. 20) is relevant for chlorpyrifos. Besides the atoms with a value of 1 in the count, chlorpyrifos contains an S atom in the molecule which is assigned the value 2 in the count:

$$T_b = 184 + 0.585\, T_m - 66.8\, \log(s) + 14.3\, N_2$$

(Eq. 3)

where: N_2 = modified count of the number of atoms (larger than H and F) in the molecule.

The data sets used in developing these equations contained a wide range of chemical structures. The method was extended by Walters et al. (1995) for compounds which can form hydrogen bonds (not relevant for the present compounds).

The boiling points estimated with the equations of Yalkowsky et al. (1994) are given in Table 3.2.

Table 3.2
Boiling points of the example compounds estimated by the method of Yalkowsky et al. (1994).

Pesticide	Melting point (K) (reference)	Value of σ	Atom count	Boiling point (K)
Chlorothalonil	525 (Tomlin, 2010)	2	$N_1 = 14$	678
Chlorpyrifos	316 (Tomlin, 2010)	1	$N_2 = 19$	641
Lindane	386 (Tomlin, 2010)	1	$N_1 = 12$	582
Pirimicarb	365 (Tomlin, 2010)	1	$N_1 = 17$	638
Quinoxyfen	380 (Tomlin, 2010)	1	$N_1 = 19$	675

3.3 Group contribution method of Simamora et al. (1993)

A method for the estimation of the boiling point of rigid aromatic compounds was developed by Simamora et al. (1993). The dataset was based on boiling points measured for 246 aromatic compounds. The statistical analysis of the contribution of atoms and groups to the molecular enthalpy of boiling ΔH_b was performed using multiple-regression programs. This resulted in a table with atom and group contributions to ΔH_b. The molecular groups in chlorothalonil were included in the table, so its boiling point could be estimated to be 684 K. The method cannot be used for the other aromatic example pesticides, because one or more groups in the molecules were missing in the table. The method is not applicable to lindane since it is not an aromatic compound.

3.4 Group contribution method of Simamora and Yalkowsky (1994)

The method of Simamora and Yalkowsky (1994) was developed for substituted aromatic compounds (including polycyclic aromates) and for heterocyclic compounds. The data set contained the measured boiling points of 444 compounds. The molecular descriptors consisted of molecular fragments (atoms, groups) and correction factors for the type of bonding. The contributions of the descriptors were calculated by regression analysis, on the basis of correlation coefficient and standard error. The descriptor contribution values for the enthalpy of boiling were presented in a table. The values are multiplied by the frequency of occurrence of the atom/group

in the molecule and all contributions are summed. The equation reads:

$$T_b = \frac{\mathsf{S}(n_i b_i)}{88}$$

where: n_i = frequency of occurrence of molecular group i;
b_i = contribution of molecular group i to the enthalpy of boiling.

The boiling point of two of the example pesticides could be estimated by the method of Simamora and Yalkowsky (1994), with the following result:
chlorothalonil: T_b = 640 K;
quinoxyfen: T_b = 699 K.
Chlorpyrifos and pirimicarb molecules contain atoms/groups not included in the table with group contributions, while lindane is not an aromatic compound.

3.5 Group contribution method of Stein and Brown (1994)

The method of Stein and Brown (1994) was developed on the basis of a data set of boiling points measured for 4426 compounds. For each of the distinguished molecular groups, the subset of compounds containing that group were selected from the total data set. The residuals between the calculated and measured boiling points were minimized in sequence for the sub-sets, resulting in updated molecular increment values for the molecular groups. About ten calculation cycles through the sub-sets were needed to obtain convergence of the group-increment values. This value is multiplied by the frequency of occurrence of the group in the molecule, after which all the contributions are summed. In this method, the group contribution method of Joback and Reid (1987) was extended by increasing the number of molecular groups from 41 to 85, e.g. by distinguishing aliphatic and aromatic groups and substituents. Further, a systematic over-estimation of higher boiling points was discovered and corrected by Stein and Brown (1994).

The first equation is used to calculate an interim value of the boiling point:

$$T_{b,\text{int}} = 198.2 + \mathsf{S}(n_i g_i)$$

where: $T_{b,\text{int}}$ = interim value of boiling temperature (K):
n_i = frequency of occurrence of group i in the molecule:
g_i = contribution of group i to the boiling point (K).

Dependent on this first result, the corrected boiling point is calculated by a second equation (two alternatives). The two equations to calculate $T_{b,\text{corr}}$ read:

$$T_{b,cor} = T_{b,\text{int}} - 94.84 + 0.5577\, T_{b,\text{int}} - 0.0007705 \left(T_{b,\text{int}}\right)^2 \quad \text{(for } T_{b,\text{int}} \leq 700\text{ K)}$$

$$T_{b,cor} = T_{b,\text{int}} + 282.7 - 0.5209\, T_{b,\text{int}} \quad \text{(for } T_{b,\text{int}} > 700\text{ K)}$$

where: $T_{b,cor}$ = corrected value of boiling temperature (K).

The group descriptions needed for four example pesticides in the present series were defined by Stein and Brown (1994). The results of the estimations are presented in Table 3.3. The thiophosphate group in chlorpyrifos was not defined, so no estimate of its boiling point could be obtained with this method.

Table 3.3
Boiling points of four example pesticides estimated by the method of Stein and Brown (1994).

Pesticide	Interim boiling point $T_{b,int}$ (K)	Corrected boiling point $T_{b,cor}$ (K)
Chlorothalonil	705	621
Lindane	469	467
Pirimicarb	724	629
Quinoxyfen	754	644

Boiling points estimated for the example pesticides with an adapted Stein and Brown (1994) method (no details), as given by ChemSpider (2010), are shown in Table 3.4.

Table 3.4
Boiling points estimated by an adapted Stein and Brown (1994) method, as given by ChemSpider (2010).

Pesticide	Boiling point (K)
Chlorothalonil	628
Chlorpyrifos	651
Lindane	578
Pirimicarb	599
Quinoxyfen	667

3.6 Selected boiling temperatures

Table 3.5 summarises the values reported and estimated for the boiling point of chlorothalonil. On the basis of the four most-specified estimates, the average value T_b = 656 K is taken as the most probable value for the boiling point of chlorothalonil. The original company report has to be checked (if possible) to see the details on the reported result (not included in the average), which is cited in two ways (i.e. 623 and > 623 K). The estimate of Chemspider (2010) is not specified.

Table 3.5
Reported and estimated values for the boiling point of chlorothalonil.

Origin	Specification	Boiling point (K)
Reported	Compilation in Table 3.1	623 and > 623
Estimated	Yalkowsky et al. (1994)	678
Estimated	Simamora et al. (1993)	684
Estimated	Simamora and Yalkowsky (1994)	640
Estimated	Stein and Brown (1994)	621
Estimated	ChemSpider (2010)	628

The values reported and estimated for the boiling point of chlorpyrifos are summarised in Table 3.6. Measurement of its boiling point does not seem to be possible because of decomposition. So only estimates are available. The value T_b = 641 K is selected for the estimations of vapour pressure because its derivation is most specified.

Table 3.6
Reported and estimated values for the boiling point of chlorpyrifos.

Origin	Specification	Boiling point (K)
Reported	Compilation in Table 3.1	Only once: > 673
Estimated	Yalkowsky et al. (1994)	641
Estimated	ChemSpider (2010)	651

Table 3.7 summarises the values reported and estimated for the boiling point of lindane. On the basis of three of the reported and estimated values at the same level, the average of T_b = 580 K is taken as the most probable value for the boiling point of lindane. The estimate according to Stein and Brown (1994) is substantially below the level of the other values; the reason for this is not clear.

Table 3.7
Reported and estimated values for the boiling point of lindane.

Origin	Specification	Boiling point (K)
Reported	Compilation in Table 3.1	561 and 597
Estimated	Yalkowsky et al. (1994)	582
Estimated	Stein and Brown (1994)	467
Estimated	ChemSpider (2010)	578

The values estimated for the boiling point of pirimicarb are summarised in Table 3.8. On the basis of the two own estimates, T_b = 634 K is taken as the most probable value for the boiling point of pirimicarb. The origin of the reported value and last estimated value is not specified.

Table 3.8
Reported and estimated values for the boiling point of pirimicarb.

Origin	Specification	Boiling point (K)
Reported	Compilation in Table 3.1	Only once: 647
Estimated	Yalkowsky et al. (1994)	638
Estimated	Stein and Brown (1994)	629
Estimated	ChemSpider (2010)	599

Table 3.9 summarises the values estimated for the boiling point of quinoxyfen. On the basis of the three own estimates, T_b = 673 K is taken as the most probable value for the boiling point of quinoxyfen. The origin of the reported value and the last estimated value is not specified.

Table 3.9
Reported and estimated values for the boiling point of quinoxyfen.

Origin	Specification	Boiling point (K)
Reported	Compilation in Table 1	Only once: 696
Estimated	Yalkowsky et al. (1994)	675
Estimated	Simamora and Yalkowsky (1994)	699
Estimated	Stein and Brown (1994)	644
Estimated	ChemSpider (2010)	667

3.7 EPI Suite method (US-EPA, 2004)

In a co-operative project, there was uncertainty on the vapour pressure of the fungicide quinoxyfen. Therefore, the normal boiling point of quinoxyfen was calculated by A. Wolters (F.Z. Jülich, personal communication) using the EPI Suite estimation program (US-EPA, 2004), that is based on an adapted Stein and Brown (1994) method. The molecular structure of the compound has to be introduced in SMILES notation (Simplified Molecular Input Line Entry System). The boiling point resulting from this calculation is 667 K for quinoxyfen. This value is used in estimating the vapour pressure of quinoxyfen (Chapter 5), to be used in computations on its volatilisation from plants (Chapter 6).

3.8 General discussion

Dearden (2003) gives a list of recent QSPR studies (1996 onward) on estimating the normal boiling point. Most of the methods were developed for specific groups of compounds, e.g. alkanes, alcohols and amines. Various methods for divergent compounds require specialised descriptions of molecular features, in combination with the use of computer programs. Types of advanced molecular descriptors are: topological, topochemical, electrotopical (Appendix I), geometrical, hydrogen-bonding, etc. The computational techniques for optimisation include linear regression, non-linear regression, multiple linear regression and neural networks. Only a few of the methods for divergent compounds allow easy calculation of the boiling point on the basis of group contributions and other easily-determined characteristics. The data set used by Dearden (2003) to test some of the software packages contained compounds with boiling points up to about 560 K. As this is distinctly lower than the boiling points of most of the present-day pesticides, these tests are not applicable here.

The development of estimation methods for physico-chemical properties of organic compounds is an area of intensive research. A selection of estimation methods has been used in the present study. More estimation methods are discussed briefly below. It is advised to try using these methods in future work on estimating the boiling point of pesticides.

Normal boiling points of organic compounds were estimated by Marrero-Morejon and Pardillo-Fontdevila (1999) by defining group-interaction contributions for the chemical structures. They found an improvement of the estimates as compared to those by the Constantinou and Gani (1994) method using the more usual group-contribution approach.

Cordes and Rarey (2002) developed a group contribution method for estimating the normal boiling point of organic chemicals. The estimations are based exclusively on the molecular structure of the compounds. Group contributions were quantified for a long list (86) of divergent structural groups. Some second-order contributions and corrections were also defined. Structural groups were usually defined including the neighbouring atoms.

The group contribution method of Cordes and Rarey (2002) for estimating the normal boiling point of organic compounds has been extended by Nannoolal et al. (2004). They defined many molecular groups and estimated their contribution (in K) to the normal boiling point. Besides, they defined second-order groups, with the corresponding correction for the boiling point. For interacting groups, group-interaction contributions were estimated. Some groups were considered to be non-additive.

Hilal et al. (2007) developed the computer program SPARC, which can calculate a wide range of physical properties of organic compounds, based on their molecular structure. They developed mechanistic perturbation models that describe the inter/intra-molecular interactions. The basis is fundamental chemical structure theory. Only the molecular structure of the compound is needed. The molecular structure can be introduced in SMILES notation or via its CAS number (Appendix I). Normal boiling point and vapour pressure are among the physical properties that can be calculated with the software.

Sanghvi and Yalkowsky (2006) calculated the normal boiling point from the ratio (enthalpy of boiling)/(entropy of boiling) (Appendix I). The enthalpy of boiling was estimated by using a group contribution method. The entropy of boiling was calculated using Trouton's Rule of constant entropy of boiling (Appendix I), modified for the flexibility (Appendix I) of the molecule and for the hydrogen bonds in the molecule. It is advised to try using this extended method in future work on estimating the boiling point of pesticides.

In an improvement of earlier group contribution methods (Joback and Reid, 1987; Constantinou and Gani, 1994), Emami et al. (2009) assumed a finite limit in the boiling temperature at infinite molecular mass. UNIFAC group contributions (see Appendix I) were taken from the ChemCAD database (Chemstations Inc, 2009). The values for the UNIFAC contributions in combination with the limit for T_b resulted in better estimates of the boiling point at higher molecular masses.

4   Reported vapour pressures

4.1   Introduction

A compilation is made of the vapour pressures reported for the five example pesticides (Tables 4.1 to 4.5). The first source of information consists of public summaries of evaluation dossiers in the framework of pesticide registration procedures (e.g. List of Endpoints). Such evaluations are based on original company reports, which are not publicly available (confidential information). The evaluations by an international organisation like UN-WHO seem to use the same type of information source. In these cases, the selected sources of information adhere as closely as possible to the original company reports. A second type of source consists of handbooks (e.g. Mackay et al., 2006b; Tomlin, 2010) and databases on the internet (e.g. ChemSpider, 2010; SRC, 2010).

4.2   Effect of temperature on vapour pressure

Vapour pressures are reported for different ambient temperatures. Direct comparison of vapour pressures is only possible after translation to a common reference temperature, in this study 293 K (20 °C). The relationship between vapour pressure and temperature can be described using the integrated Clausius-Clapeyron equation (Staikova et al., 2005; Mackay et al., 2006a):

$$\frac{P_v}{P_{v,ref}} = \exp\left[\frac{\Delta H_v}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \qquad \text{(Eq. 8)}$$

where: P_v =   vapour pressure (mPa) at temperature T
                 $P_{v,ref}$ =   vapour pressure (mPa) at reference temperature T_{ref}
                 ΔH_v =   molar enthalpy of vaporisation (J mol^{-1})
                 R   =   molar gas constant (8.314 J mol^{-1} K^{-1})
                 T   =   temperature of measurement/estimation (K)
                 T_{ref} =   reference temperature (K)

Smit et al. (1997) compiled values for the molar enthalpy of vaporisation, ΔH_v, reported in the literature and they calculated additional values of this quantity from other published vapour pressure measurements at different temperatures. The average value of ΔH_v for a series of nineteen pesticides was calculated to be 95 kJ mol^{-1}. This value was used as default value for the vapour pressure - temperature relationship in cases in which no specific value of ΔH_v for the pesticide was available. Using the default value of ΔH_v means that the vapour pressure at 293 K is 0.52 times that at 298 K.

4.3   Vapour pressure of solid and sub-cooled liquid states

Several pesticides have a melting point above the environmental temperatures. The vapour pressure above the solid (crystalline) state of a compound is lower than that above the sub-cooled liquid state at the same temperature. This is illustrated in Figure 1 for water. It is important to check (if possible) for which state the vapour pressure of a pesticide is reported.
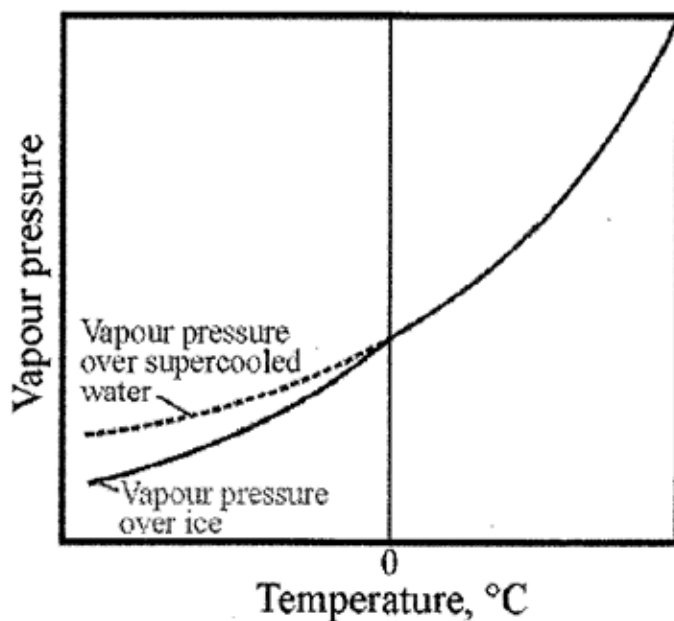
Figure 1
Vapour pressure - temperature relationships for liquid, sub-cooled liquid and solid states, illustrated for water.

Various estimation methods for the vapour pressure take the difference in state of a compound into account (Chapter 5). Some other methods were developed for both the liquid and solid states (Chapter 5). However, in some cases the vapour pressure estimation method holds for the sub-cooled liquid state, whereas the five example pesticides are solids at ambient temperatures (see the melting points in Table 3.1). The ratio between the vapour pressures for the solid and sub-cooled liquid states can be calculated (Mackay et al., 1982; Mackay et al., 2006a) by:

$$\ln\left(\frac{P_{v,s}}{P_{v,l}}\right) = -\frac{\Delta S_m}{R}\left(\frac{T_m}{T} - 1\right)$$

(Eq. 9)

where $P_{v,s}$ = vapour pressure above the solid state (mPa)
  $P_{v,l}$ = vapour pressure above the sub-cooled liquid state (mPa)
  ΔS_m = molar entropy of melting (J mol^{-1})
  R = molar gas constant (8.314 J mol^{-1} K^{-1})
  T_m = melting temperature (K)
  T = temperature of measurement/estimation (K)

The standard value of $\Delta S_m/R = 6.8$ was derived by Mackay et al. (1982) for compounds with short aliphatic chains (default value in Mackay et al., 2006a). The improved value of $\Delta S_m/R = 7.9$, derived as average value for four carbamate pesticides (Tsuzuki, 2001), is used as default value in the present study.

An equation for calculating the vapour pressure above the solid state from that above the sub-cooled liquid state is presented by Moller et al. (2008):

$$\ln(P_{v,s}) = \ln(P_{v,l}) - \frac{\Delta H_m}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)$$

(Eq. 10)

where: $P_{v,s}$ = vapour pressure above the solid state (mPa)

$P_{v,l}$ = vapour pressure above the liquid state (mPa)

$\mathrm{D}H_m$ = molar enthalpy of melting (J mol^{-1})

R = molar gas constant (8.314 J mol^{-1} K^{-1})

T = temperature (K)

T_m = melting temperature (K)

This equation is obtained by combining Eq. 9 with the equation $\Delta S_m = \Delta H_m/T_m$ (Waser, 1966). Now the calculation requires both the melting temperature and the molar enthalpy of melting of a compound as input. As the latter quantity requires additional estimation, the use of Equation 9 is preferred in this study.

In cases in which no description of the procedure is available, it is assumed that the vapour pressure holds for the solid state of a compound (applicable to ambient temperatures). By using some methods, e.g. gas-liquid chromatography, the vapour pressure for the liquid state is obtained. In this method, the retention times of the studied compound and a series of reference compounds (with known vapour pressure-temperature relationship) in a gas-liquid chromatography set-up at high temperatures are measured. The vapour pressure of the studied compound is calculated from the retention times and from the known vapour pressures. Such results are translated to the value for the solid state of the compound (Eq. 9) before inclusion in the last column of Tables 4.1 to 4.5.

4.4   Vapour pressures reported for chlorothalonil

In various cases, the same vapour pressure has been cited for chlorothalonil (Table 4.1). Presumably, the same company report was cited here. The very wide range of values given by Mackay et al. (2006b) illustrates the confusion about the level of the vapour pressure of chlorothalonil in the past. One published value (Goel et al., 2007) is somewhat lower than the value cited repeatedly. Comparison with estimated vapour pressures (follows in Chapter 5) is desirable for chlorothalonil, because there seem to be only few original data of reasonable quality.

Table 4.1

Vapour pressures reported for chlorothalonil. Translated (if needed) to the reference temperature of 293 K (using $\Delta H_v = 95$ kJ mol^{-1}) and to the solid state (Eq. 9) at 293 K.

Vapour pressure (mPa) at temperature	Reference	Origin or method	Vapour pressure (mPa) translated to 293 K
0.076 at 298 K	UN-WHO (1996)	Company reports	0.040
0.076 at 298 K	NL-Ctgb (2001)	Draft EU Monograph	0.040
0.076 at 298 K	EC-DGHC (2006a)	Company reports	0.040
Very wide range of values	Mackay et al. (2006b)	Handbooks	
0.076 at 298 K	Tomlin (2010)	Origin not given	0.040
5.81 and 0.076 at 298 K	ChemSpider (2010)	Not given	3.02 and 0.040
0.076 at 298 K	SRC (2010)	Tomlin (2003)	See Tomlin (2010)
0.053 at 298 K	Goel et al. (2007)	GC method	0.028

4.5 Vapour pressures reported for chlorpyrifos

Three values of the vapour pressure of chlorpyrifos (presumably) cited from company reports are close to each other (Table 4.2). These values may originate from the same company report, with only small differences in translation factors.

Table 4.2

Vapour pressures reported for chlorpyrifos. Translated (if needed) to the reference temperature of 293 K (Eq. 8, using ΔH_v = 95 kJ mol[1]) and to the solid state (Eq. 9) at 293 K.

Vapour pressure (mPa) at temperature	Reference	Origin or method	Vapour pressure (mPa) translated to 293 K
2.49 at 293 K	US-EPA (2002)	Merck Index	2.49
1.43 at 293 K	EC-DGHC (2005a)	Company reports	1.43
3.35 at 298 K			
1.43 at 293 K	NL-Ctgb (2009)	EU monograph	1.43
3.35 at 298 K			
2.7 at 298 K	Tomlin (2010)	Origin not given	1.40
2.49 at 298 K	Neely & Blau (1976)	Not given	1.29
2.7 at 298 K	Racke (1993)	Company report	1.40
0.88 at 293 K (liquid state)	Kim et al. (1984)	GC method	0.52
< 6.7 at 298 K (liquid state)	Hinckley (1990)	GC method	< 1.9
2.19 at 298 K (liquid state)	Donovan (1996)	GC method	0.63
2.97 mPa at 298 K (liquid state)	Tsuzuki (2000)	Estimation method	0.85
Range of values roughly at the same level	Mackay et al. (2006b)	Handbooks and literature	
2.17 and 2.71 at 298 K	ChemSpider (2010)	Not given	1.13 and 1.41
2.71 at 298 K	SRC (2010)	Tomlin (1997)	See Tomlin (2010)

The vapour pressure of chlorpyrifos was determined by Kim et al. (1984) using a gas chromatographic method. Comparison of its GLC retention time with those of reference compounds with known vapour pressure, resulted in a vapour pressure of 0.88 mPa at 293 K (liquid state). Translation of this value to the solid state (Eq. 9), resulted in a vapour pressure of 0.52 mPa at 293 K for chlorpyrifos (Table 4.2).

Hinckley (1990) determined the vapour pressure of chlorpyrifos by using a gas chromatographic method. The result of < 6.7 mPa at 298 K applied to the liquid state. The symbol < is added because the method was found to over-estimate the vapour presure of a series of organophosphate pesticides. Translation of the result to the solid state (x 0.55; Eq. 9) and to the reference temperature (x 0.52; Eq. 8 with ΔH_v = 95 kJ mol^{-1}) gives a vapour pressure of < 1.9 mPa at 293 K for chlorpyrifos (Table 4.2).

The vapour pressure of chlorpyrifos was measured also by Donovan (1996) using a gas chromatographic method. He obtained a vapour pressure of 2.19 mPa at 298 K, which holds for the sub-cooled liquid state. Translation of the result to the solid state (x 0.55; Eq. 9) and to the reference temperature (x 0.52; Eq. 8 using ΔH_v = 95 kJ mol^{-1}) yields a vapour pressure for chlorpyrifos of 0.63 mPa at 293 K (Table 4.2).

First of all, Tsuzuki (2000) refers to the gas chromatographic determination of the vapour pressure of chlorpyrifos by his company as published by Donovan (1996, see above). The modified Watson method (OECD, 1995), based on the normal boiling point, was optimised by Tsuziki (2000) for the estimation of the vapour pressure of organophosphate pesticides. The optimisation involved improved parameter estimation for specific groups and bonds in the organophosphate molecules. He obtained the following two estimates of the vapour pressure of liquid chlorpyrifos at 298 K: 1.86 mPa (using Sugden's parachor) and 4.07 mPa (using

McGowan's parachor) (a description of parachor is given in the Appendix I). When the average value of 2.97 mPa is translated to the solid state (x 0.55; Eq. 9) and to the reference temperature (x 0.52; Eq. 8 using ΔH_v = 95 kJ mol^{-1}), this results in an estimated vapour pressure of 0.85 mPa at 293 K for chlorpyrifos (Table 4.2).

Two vapour pressures obtained for chlorpyrifos by the GC method in published studies and one estimated value are lower than the values derived from company reports (Table 4.2). The average of the published vapour pressures (0.67 mPa at 293 K) is 0.49 times the average of the cited vapour pressures (1.36 mPa). Without studying the details of the procedure used by the company (confidential information), selection of the most probable value is not possible. The use of additional estimation methods could be helpful here.

The vapour pressure of chlorpyrifos(-ethyl) (Table 4.2) is somewhat lower than that of chlorpyrifos-methyl (3.0 mPa at 298 K; EC-DGHC, 2005b; Tomlin, 2010), as expected. Translation to 293 K by calculation gave 1.95 mPa for chlorpyrifos-methyl (EC-DGHC, 2005b).

4.6 Vapour pressures reported for lindane

A range of vapour pressures from e.g. 1.25 to 4.34 mPa at 293 K is included in the evaluations for lindane (Table 4.3). For that reason, the published studies as described below are welcome in the selection of the most probable vapour pressure for lindane.

Table 4.3

Vapour pressures reported for lindane. Translated (if needed) to the reference temperature of 293 K (Eq. 8, for ΔH_v see text) and to the solid state (Eq. 9) at 293 K.

Vapour pressure (mPa) at temperature	Reference	Origin or method	Vapour pressure (mPa) translated to 293 K
4.34 at 293 K	UN-WHO (1991)	Company reports	4.34
Wide range of values, e.g. measurement of 4.4 at 297 K	NL-RIVM (1992)	Company reports	e.g. 2.60
1.25 at 293 K	US-EPA (2001)	Company reports	1.25
4.4 at 297 K	Tomlin (2010)	Origin not given	
> 1.25 at 293 K	Balson (1947)	Effusion method	> 1.25
4.34 at 293 K	Spencer & Cliath (1970)	Gas saturation	4.34
86.1 at 298 K (liquid state)	Bidleman (1984)	GC method	3.66
55.2 and 64.9 at 298 K (liquid state)	Hinckley et al. (1990)	GC method	2.78 and 3.27
9.4 at 293 K	Wania (et al. (1994)	Gas saturation	9.4
3.83 at 293 K	Boehncke et al. (1996)	Effusion method	3.83
10.4 at 298 K	Giustini et al. (1998)	Effusion method	5.50
4.5 at 293 K	Xiao et al. (2004)	Critical evaluation	4.5
Wide range of values	Mackay et al. (2006b)	Handbooks and literature	
(555 at 298 K and) 4.69 at 298 K	ChemSpider (2010)	Not given	2.44
5.6 at 293 K	SRC (2010)	Tomlin (1997)	5.6

Balson (1947) used the effusion method to measure the vapour pressure of some pesticides and related compounds. His results for lindane corresponded to a vapour pressure of 1.25 mPa at 293 K (Table 4.3). In the comparison with a higher vapour pressure for lindane obtained later on, Spencer and Cliath (1970) concluded that the concentration in the effusion cavity must have been unsaturated (was not checked). This led

to under-estimation of the vapour pressure, so the result of Balson (1947) is provided with the symbol > in Table 4.3.

The vapour pressure of lindane was measured by Spencer and Cliath (1970) using the gas saturation method, which is suitable for low-volatile compounds. They obtained a vapour pressure of 4.34 mPa at 293 K (Table 4.3).

Bidleman (1984) measured the vapour pressure of lindane by using a gas chromatographic method. The average of the two values obtained with different GC columns was 86.1 mPa at 298 K. This result applies to the sub-cooled liquid state. Translation of the result to the solid state (x 0.082; Eq. 9) and to the reference temperature (x 0.52; Eq. 8 using ΔH_v = 95 kJ mol^{-1}) gives a vapour pressure for lindane of 3.66 mPa at 293 K (Table 4.3).

The vapour pressure of lindane as a function of the temperature was measured by Boehncke et al. (1996) using the Knudsen effusion technique. This resulted in a vapour pressure of 3.83 mPa at 293 K (solid state) (Table 4.3).

Giustini et al. (1998) measured vapour pressures of lindane in a range of temperatures above 320 K, by using torsion-effusion and Knudsen-effusion methods. On the basis of all measuring results, the molar enthalpy of vaporisation ΔH_v was calculated to be 92.4 kJ mol^{-1}. Vapour pressure was extrapolated downwards to 10.4 mPa at 298 K. Using these data, vapour pressure can be extrapolated further downwards to 5.50 mPa at the reference temperature of 293 K (Table 4.3).

Xiao et al. (2004) investigated the reliability and consistency of reported physico-chemical properties of lindane. On the basis of literature data, they derived a specific value of $\Delta S_m/R$ = 7.36 for lindane (Eq. 9), which implies that the ratio $P_{v,s}/P_{v,l}$ = 0.097 at 293 K. A consistent and reliable vapour pressure derived from critically evaluated reported values was $P_{v,s}$ = 4.5 mPa at 293 K (solid state) (Table 4.3).

Five published studies on the vapour pressure of lindane indicate that some of the values in the registration evaluations (Table 4.3) are too low. The vapour pressure of 4.5 mPa at 293 K, as resulting from the critical study of Xiao et al. (2004), is considered to be the most probable value. This value is close to the average (4.3 mPa at 293 K) of four published experimental vapour pressures (Table 4.3).

4.7 Vapour pressures reported for pirimicarb

The vapour pressure of pirimicarb was measured by Tsuzuki (2001) using a gas chromatographic method. The factor for the translation from sub-cooled liquid state to solid state (Eq. 9) is 0.144. The result of 7.4 mPa (liquid state, 298 K) thus corresponds to a vapour pressure of 0.56 mPa for the solid state at 293 K (Table 4.4). The modified Watson estimation method (OECD, 1995) was optimised for carbamates by Tsuzuki (2001). The result for pirimicarb of 2.95 mPa (liquid state, 298 K) corresponds to a vapour pressure of 0.22 mPa for the solid state at 293 K (Table 4.4).

Table 4.4

Vapour pressures reported for pirimicarb. Translated (if needed) to the reference temperature of 293 K (Eq. 8, using ΔH$_v$ = 95 kJ mol^{1}) and to the solid state (Eq. 9) at 293 K.

Vapour pressure (mPa) at temperature	Reference	Origin or method	Vapour pressure (mPa) translated to 293 K
4.0 at 303 K	NL-RIVM (1989)	Company reports	1.11
0.43 at 293 K	EC-DGHC (2006b)	Company reports; by interpolation	0.43
0.43 at 293 K	Tomlin (2010)	By interpolation Origin not given.	0.43
7.4 at 298 K (liquid state)	Tsuzuki (2001)	GC method	0.56
2.95 at 298 K (liquid state)	Tsuzuki (2001)	Estimated	0.22
0.97 and 4.0 at 298 K	Mackay et al. (2006b)	Handbooks	
1.20 and 0.97 at 298 K	ChemSpider (2010)	Not given	
0.97 at 298 K	SRC (2010)	Tomlin (1997), extrapolated	See Tomlin (2010)

The two values published for the vapour pressure of pirimicarb indicate that the value of 1.11 mPa at 293 K in Table 4.4, cited from the company reports, is of the right order of magnitude. However, selection of the most probable vapour pressure requires evaluation of the quality of the company study.

4.8   Vapour pressures reported for quinoxyfen

The two values for the vapour pressure of quinoxyfen included in Table 4.5 are mostly the same: they seem to originate from the same company report. As the method of determination in not available and there are no other measurements, estimation of the vapour pressure of quinoxyfen is highly desirable (Chapter 5). Volatilisation loss of quinoxyfen from bean plants was reported to be 5% of the dosage, but higher volatilization was considered to be possible (EC-DGHC, 2003). The volatilisation of quinoxyfen in relation to its vapour pressure is discussed further in Chapter 6.

Table 4.5

Vapour pressures reported for quinoxyfen. Translated (if needed) to the reference temperature of 293 K (Eq. 8, using ΔH$_v$ = 95 kJ mol^{1}) and to the solid state (Eq. 9) at 293 K.

Vapour pressure (mPa) at temperature	Reference	Origin or method	Vapour pressure (mPa) translated to 293 K
0.012 at 293 K 0.020 at 298 K	EC-DGHC (2003)	Company reports	0.012
0.012 at 293 K 0.020 at 298 K	NL-Ctgb (2005)	EU-Monograph	0.012
0.012 at 293 K 0.020 at 298 K	Tomlin (2010)	Origin not given	0.012
0.075 and 0.02 at 298 K	ChemSpider (2010)	Not given	
0.020 at 298 K	SRC (2010)	Tomlin (2003)	

4.9   Concluding remarks

Evaluations and handbooks/databases are main sources of information on the vapour pressure. In many cases they seem to refer to the same original report, not available publicly. In the cases of chlorpyrifos and lindane,

various determinations of vapour pressure were published in the literature. Published measurements are scarce for chlorothalonil and pirimicarb (one reference for each). For quinoxyfen, not any determination of vapour pressure could be found in the published literature. In cases of conflicting data or when information is scarce, the use of estimation methods (Chapter 5) may be helpful in diminishing the uncertainty on the vapour pressure.

5 Estimating vapour pressures

5.1 Introduction

The vapour pressures of pesticides can be estimated using Quantitative Structure Property Relationship (QSPRs). A list of QSPR studies (from 1990 onward) on estimating the vapour pressure of organic compounds has been given by Dearden (2003). Various methods were developed for specific chemical groups, e.g. hydrocarbons and halogenated hydrocarbons. A series of methods for a diversity of compounds (belonging to different chemical classes) require specialised description of molecular features, in combination with the use of computer programs. Types of advanced molecular descriptors are: topological, topochemical, electrotopological (Appendix I), hydrogen-bonding, etc. The computational techniques for optimisation include multiple linear regression, multifunctional autocorrelation and neural networks. Only a limited number of the methods for divergent compounds allow simple calculation of the vapour pressure on the basis of molecular-group contributions and easily-determined characteristics.

Various estimation methods have been developed for compounds (industrial chemicals) having much higher vapour pressures than most pesticides. Extrapolation by using such estimation methods below the range of vapour pressures used in development may be expected to give inaccurate results. Therefore, methods developed for compounds with high vapour pressures only are excluded from the present study.

In this chapter, a short series of relevant easy-to-use calculation methods is described and applied to estimating the vapour pressure of the five example pesticides.

5.2 Boiling point method of Mackay et al. (1982)

Equations for estimating the vapour pressure of hydrophobic compounds like hydrocarbons and halogenated hydrocarbons were developed by Mackay et al. (1982). They recommended the use of the KLH equation. K stands for the use of Kistiakowsky's equation for $\Delta H_b/T_b$, with ΔH_b = molar enthalpy of vaporisation at the boiling temperature T_b. LH refers to the Linear relationship between ΔH_v (molar enthalpy of vaporisation) and temperature T, in the range below boiling temperature T_b. A special term with melting temperature T_m is included to account for the possible solid state of the compound at ambient temperatures, which reduces the vapour pressure as compared to that of the subcooled-liquid state at the same temperature.

The data set used for development (Mackay et al., 1982) consisted of data for 72 hydrophobic compounds of environmental interest (melting temperature, boiling temperature, vapour pressure at 298 K). The boiling points ranged up to 568 K, which is below the boiling point of most of the example pesticides (Table 3.1). The best value of coefficient K in the linear relationship between ΔH_v and temperature was found to be 0.803.

The final KLH equation recommended by Mackay et al. (1982) for the calculation of the vapour pressure at environmental temperature T (K) from the boiling and melting temperatures reads:

$$\ln(p_v) = -(4.4 + \ln(T_b))\left[1.803\left(\frac{T_b}{T} - 1\right) - 0.803\ln\left(\frac{T_b}{T}\right)\right] - 6.8\left(\frac{T_m}{T} - 1\right) \qquad \text{(Eq. 11)}$$

where: p_v = vapour pressure (atm)
  T_b = boiling temperature (K)
  T_m = melting temperature (K)
  T = temperature of interest (K).

The last term including the melting point is ignored for liquids at temperature T.

The method was developed for hydrocarbons and halogenated hydrocarbons, without polar groups. The range of boiling points in the data set used for development was 373-568 K, the maximum of which is lower than the boiling point of many pesticides. Burkhard et al. (1985) found that the Mackay et al. (1982) method overestimated the vapour pressures of a series of polychlorinated biphenyls (PCB's): on average by a factor of 8 for four compounds with three to five Cl-atoms.

The results of estimating the vapour pressure of the five example pesticides with the method of Mackay et al. (1982) are given in Table 5.1. Because the vapour pressure is likely to be over-estimated with this method, the symbol < is placed before the values.

Table 5.1

Vapour pressure of the example pesticides estimated with the method of Mackay et al. (1982).

Pesticide	Estimated vapour pressure (mPa) at 293 K
Chlorothalonil	< 0.015
Chlorpyrifos	< 4.47
Lindane	< 23.9
Pirimicarb	< 2.06
Quinoxyfen	< 0.16

5.3 Boiling point + structure method of Mishra and Yalkowsky (1991)

A vapour pressure estimation equation based on melting temperature, boiling temperature, rotational symmetry number and conformational flexibility number was developed by Mishra and Yalkowsky (1991). They used the same data set of 72 compounds as Mackay et al. (1982). Factors σ for rotational symmetry and φ for flexibility of the molecular structure (Appendix I) were included in the equation. The σ and φ values assigned to the 72 molecules in the dataset were given in a table.

The equation reads:

$$\ln(p_v) = -\left(\frac{T_m - T}{T}\right)(8.5 - 5.0\log(\sigma) + 2.3\log(\varphi)) - \frac{T_b - T}{T}(10 + 0.08\log(\varphi)) +$$

(Eq. 12)

$$+\left(\frac{T_b - T}{T} - \ln\left(\frac{T_b}{T}\right)\right)(-6 - 0.9\log(\varphi))$$

where: p_v = vapour pressure (atm)
  T_m = melting point (K)
  T = temperature of interest (K)
  σ = rotational symmetry number
  φ = molecular flexibility number
  T_b = boiling point (K)

Specifications on the derivation of values for the symmetry and flexibility numbers were given by Jain and Yalkowsky (1999). The results of the estimations with the method of Mishra and Yalkowsky (1991) for the five example pesticides are given in Table 5.2. In the test of this equation by Myrdal and Yalkowsky (1997) it was found that this equation overestimated low vapour pressures. Therefore, the results of the estimations given in Table 5.2 are preceded by the < symbol.

Table 5.2

Results of estimating the vapour pressure of the five example pesticides using the method of Mishra and Yalkowsky (1991).

Pesticide	Rotational symmetry number, σ	Molecular flexibility number, φ	Estimated vapour pressure (mPa) at 293 K
Chlorothalonil	2	1	< 0.12
Chlorpyrifos	1	1	< 32.6
Lindane	1	1	< 64.1
Pirimicarb	1	1	< 10.5
Quinoxyfen	1	1	< 1.16

5.4 Boiling point + structure method of Myrdal and Yalkowsky (1997)

In the study of Myrdal and Yalkowsky (1997), the earlier method of Mishra and Yalkowsky (1991) was improved. More complex organic compounds were included in the method-development set and better estimates were made for the parameters. Modifications were made in the terms for the entropy of boiling and the heat capacity change upon boiling. The data set consisted of 300 diverse compounds with known melting point, boiling point and vapour pressure. The set included compounds with vapour pressures around 1 mPa and lower.

In the estimation equation the term for hydrogen bonds can be omitted, because this type of bonding is not relevant for the example pesticides. Then the equation reads:

$$\log(p_v) = -\frac{[56.5 - 19.2\log(s) + 9.2t](T_m - T)}{19.1T} - \frac{[86.0 + 0.4t](T_b - T)}{19.1T} +$$
$$+ \frac{[-90.0 - 2.1t]}{19.1}\left[\frac{T_b - T}{T} - \ln\left(\frac{T_b}{T}\right)\right]$$

(Eq.13)

where: p_v = vapour pressure (atm)
σ = rotational symmetry number
τ = effective number of torsional bonds
T_m = melting temperature (K)
T_b = boiling temperature (K)
T = temperature of interest (K)

The equation appeared to be appropriate for both liquids and solids. There was no systematic deviation in the estimates of low vapour pressures, compared to the measured values.

The vapour pressures of the example pesticides estimated with the method of Myrdal and Yalkowsky (1997) are given in Table 5.3.

Table 5.3
Vapour pressure of the example pesticides estimated with the method of Myrdal and Yalkowsky (1997).

Pesticide	Rotational symmetry number σ	Effective number of torsional bonds, τ	Estimated vapour pressure (mPa) at 293 K
Chlorothalonil	2	0	0.019
Chlorpyrifos	1	5	1.00
Lindane	1	0	18.1
Pirimicarb	1	2.5	0.53
Quinoxyfen	1	1	0.089

5.5 Group contribution method of Simmons (1999)

The vapour pressure calculation method described by Simmons (1999) is based on the molecular structure of the compound and on its melting point. It is a group contribution method, which can deal with a large number and a large variety of molecular fragments. The data set consisted of 1410 compounds, which were described by 94 molecular fragments. The vapour pressures cover a wide range; low vapour pressures around 0.01 mPa were included. A term is added to the equation to account for the vapour pressure to be lower above the solid state than above the sub-cooled liquid state at the same temperature. This term applies to compounds with a melting point higher than ambient temperature. Unfortunately, the data set was rather old and the quality of the data was not checked.

The estimation equation reads as follows:

$$\log(vp) = \sum (a_i f_i) - \frac{1.56\,(t_m - 25)}{100} + 4.42 \qquad \text{(Eq. 14)}$$

where: vp = vapour pressure (mmHg) at 25 °C
a_i = contribution of molecular fragment i
f_i = number of molecular fragments i in the molecule
t_m = melting point (°C).

The coefficients a_i are given in a large table, which contains all the molecular fragments needed for the five example pesticides. Alifatic and aromatic substituents are distinguished. The method provided reasonable estimates (comparison in a graph) of the vapour pressure of 20 agrochemicals (Simmons, 1999).

The results of the estimation of the vapour pressure of the five example pesticides by the method of Simmons (1999) are presented in Table 5.4. The original estimates for 298 K were translated to the values at 293 K, using Eq. 8 with a molar enthalpy of vaporisation ΔH_v of 95 kJ mol^{-1} (Smit et al., 1997).

Table 5.4

Vapour pressure of the five example pesticides estimated by the method of Simmons (1999) and subsequently translated to 293 K.

Pesticide	Estimated vapour pressure (mPa) at 293 K
Chlorothalonil	0.0013
Chlorpyrifos	0.71
Lindane	6.4
Pirimicarb	0.38
Quinoxyfen	0.0060

5.6 Group contribution method of Jain and Yalkowsky (1999)

The UPPER scheme (Unified Physical Property Estimation Relationships) can be used to calculate various physical properties (Jain and Yalkowsky, 1999), among which vapour pressure. Molecular group contribution values are given in a table and these are added up for the whole molecule. Two additional parameters are used: the molecular symmetry number and the molecular flexibility number. The method is described for aromatic compounds with a limited number of substituents. The vapour pressures in the data set used for development range down to below 1 mPa.

Unfortunately, the method cannot be used for the four aromatic example pesticides, because essential substituents are missing in the list (no group contribution given). Moreover, the method does not apply to lindane (not an aromatic compound). The method is only usable for comparatively simple aromatic compounds with methyl-, halogen- and nitro-groups as substituents.

5.7 Comparison of estimates with reported vapour pressures

Reported and estimated values of the vapour pressure of **chlorothalonil** are collected in Table 5.5. The estimate given by ChemSpider (2010) using a modified Grain method is included. There is only one reported value: that cited from company reports (see Table 4.1). Most of the estimation methods indicate that the vapour pressure reported for chlorothalonil (without information on the procedure) is of the right order of magnitude. The vapour pressure estimated by the method of Simmons (1999) is very low, as compared to the other values. It should be noted that also much higher vapour pressures of chlorothalonil (up to 232 Pa at 298 K) were reported in the past (Mackay et al., 2006b).

Table 5.5

Vapour pressures (at 293 K) reported and estimated for chlorothalonil.

		Vapour pressure (mPa) at 293 K
Value cited from company reports		0.040
Estimation method	Modified Grain method (ChemSpider, 2010)	0.033
	Mackay et al. (1982)	< 0.015
	Mishra and Yalkowsky (1991)	< 0.12
	Myrdal and Yalkowsky (1997)	0.019
	Simmons (1999)	0.0013

The vapour pressure reported for **chlorpyrifos** (Table 5.6) is taken to be the value of 1.43 mPa (at 293 K) in the most recent registration evaluation (Table 4.2), that of EC-DGHC (2005a). The average value of 0.67 mPa from the published studies is included in Table 5.6. The five estimated values indicate that the reported and published vapour pressures are of the right order of magnitude. In the comparison between the published values and the three most specific estimates, it should be noted that an uncertainty of about a factor of 2 in the vapour pressure is considered to be small.

Table 5.6

Vapour pressures (293 K) reported, published and estimated for chlorpyrifos.

		Vapour pressure (mPa) at 293 K
Value cited from company reports		1.43
Average of three published studies (Table 4.2)		0.67
Estimation method	Modified Grain method (ChemSpider, 2010)	1.42
	Mackay et al. (1982)	< 4.47
	Mishra and Yalkowsky (1991)	< 32.6
	Myrdal and Yalkowsky (1997)	1.00
	Simmons (1999)	0.71

Several studies were carried out and published on the vapour pressure of **lindane** (Table 4.3). The value of 4.5 mPa at 293 K is considered to be the most probable value. This value is included with the estimates in Table 5.7. In this case, the results of the estimation methods do not provide additional certainty to the experimentally obtained values of the vapour pressure. All approaches agree in the indication that lindane has highest vapour pressure of the five example pesticides.

Table 5.7

Vapour pressures (at 293 K) published and estimated for lindane.

		Vapour pressure (mPa) at 293 K
Most probable published value (Table 4.3)		4.5
Estimation methods	Modified Grain method (ChemSpider, 2010)	35.0
	Mackay et al. (1982)	< 23.9
	Mishra and Yalkowsky (1991)	< 64.1
	Myrdal and Yalkowsky (1997)	18.1
	Simmons (1999)	6.4

Reported, published and estimated vapour pressures of **pirimicarb** are given in Table 5.8. The two published values and the estimated values indicate that the vapour pressure cited from the company is of the right order of magnitude. Again it should be noted that an uncertainty of about a factor of 2 is considered to be small for the vapour pressure of a pesticide.

Table 5.8

Vapour pressures (at 293 K) reported, published and estimated for pirimicarb.

		Vapour pressure (mPa) at 293 K
Value cited from company reports		1.11
Published values		0.22
		0.56
Estimation method	Modified Grain method (ChemSpider, 2010)	7.7
	Mackay et al. (1982)	< 2.06
	Mishra and Yalkowsky (1991)	< 10.5
	Myrdal and Yalkowsky (1997)	0.53
	Simmons (1999)	0.38

In future work it can be attempted to use the group contribution method of Pankow and Asher (2008) for oxygenated and nitrogen-containing compounds for estimating the vapour pressure of pirimicarb.

The vapour pressure of **quinoxyfen**, as cited from company reports (Table 4.5), is 0.012 mPa at 293 K (included in Table 5.9). No published experiments are known for this pesticide. The results of the estimates made with the present methods, included in Table 5.9, do not give the same indication of the correctness of the order of magnitude of the reported value. One of the specific estimates is higher and the other is lower than the reported value. The estimation methods confirm that the vapour pressure of quinoxyfen can be expected to be very low, although there is much variation in the value.

Table 5.9

Reported and estimated vapour pressures of quinoxyfen.

		Vapour pressure (mPa) at 293 K
Value cited from company reports		0.012
Estimation method	Modified Grain method (ChemSpider, 2010)	0.13
	Mackay et al. (1982)	< 0.16
	Mishra and Yalkowsky (1991)	< 1.16
	Myrdal and Yalkowsky (1997)	0.089
	Simmons (1999)	0.006
	EPI Suite program (US-EPA, 2004)	0.13

The vapour pressure of quinoxyfen at 298 K was calculated by A. Wolters (FZ Jülich, personal communication) using the EPI Suite estimation program (US-EPA, 2004). This program is based on a modified Grain method and it is the preferred method in EPI Suite for compounds which are solid at ambient temperatures. The molecular structure of the compound has to be introduced in SMILES notation (Simplified Molecular Input Line Entry System). The melting point of 380 K for quinoxyfen was introduced as given by Tomlin (2003). The vapour pressure resulting from this calculation is 0.247 mPa (at 298 K). Using Eq. 8 with a molar enthalpy of volatilisation ΔH_v of 95 kJ mol^{-1}, this can be translated to a vapour pressure of 0.13 mPa at 293 K (Table 5.9). [Using the vapour pressure calculation in the EPI Suite program without introduction of the melting point of quinoxyfen results in a vapour pressure of 0.088 mPa at 298 K, which corresponds to 0.046 mPa at 293 K].

The values in Table 5.9 illustrate that the vapour pressure of quinoxyfen is lower than those of the other four five example pesticides. It can be expected that both measurement and estimation of the vapour pressure is more difficult as the level of the vapour pressure is lower.

5.8 General discussion

The type and extent of information on the vapour pressure of a pesticide can be highly different. For some old pesticides, like lindane, a series of determinations have been published. The values published from 1970 onwards are at the same level. In one of the latest registration evaluations (US-EPA, 2001), an old vapour pressure (too low) is included. In the case of careful and published determinations, like those for lindane, the estimation methods do not provide additional certainty on the vapour pressure.

The results of a few published studies are available for pesticides like chlorpyrifos and pirimicarb. The results of the most specific estimation methods are at the same level as that of the published vapour pressures. The level in the additional information is somewhat lower than cited from the company reports (confidential). Only by studying the procedure in the company reports, progress can be made in the selection of the most probable vapour pressure. The uncertainty in vapour pressure seems to be limited to a factor of 2 for chlorpyrifos but it is greater for pirimicarb.

The establishment of the most probable vapour pressure is most difficult for a pesticide like quinoxyfen. The company report is not available (confidential) and there are no published studies. Moreover, the most specific estimation methods give both higher and lower values than reported. Both measurements and estimations of low vapour pressures yield uncertain results: only a wide range of possible vapour pressures can be derived. Although the estimation methods (Table 5.9) contain the atoms/groups in the quinoxyfen molecule, evaluation of their relative suitability is expected to be difficult. Quinoxyfen is a rather specific compound; it does not belong to a well-studied series of related compounds. Because of the uncertainty, substances like quinoxyfen with low vapour pressure (e.g. in the range of 0.01 to 0.1 mPa at 293 K) will often be not suitable for use in the testing of models for volatilisation from crops. Nevertheless, even at such low vapour pressures a substantial fraction of the pesticide dosage can volatilise, especially in case of a rather persistent deposit at the plant surface.

In an earlier study, Marino (2006) collected values for physical properties of a wide range of organic chemicals from different sources, both measured and estimated values. If at least three values of a physical property were available (from the eight sources), they were included in the analysis of the differences. The ratios for the maximum to minimum values of the normal boiling point (in K) were within a factor of two (which is high for the boiling point). In about 40% of the cases, the range of maximum to minimum values for the vapour pressure (in mm Hg at 298 K) spanned more than an order of magnitude. These results confirm that the most reliable value of a physical property of an organic compound should be selected with care, using all the information and methods available.

A survey of types of estimation methods for physico-chemical properties of organic chemicals has been given recently by Joback (2009). The group-contribution type of method seems to be most suitable for the use by non-specialists. Only the molecular structure of the compound is required for this type of method. More specialized methods could be used if included in a software package, with easy entry of readily- available input data.

Moller et al. (2008) extended a group-contribution method for estimating vapour pressures of organic compounds, making it more suitable for low-volatile compounds. They defined both group contributions and group interactions, the latter for hydrogen-bonding groups. A long list of divergent structural and functional

groups, with their contribution and interaction values, was presented. The boiling point of the compound must be known. It is recommended to try using this method in future work on the vapour pressure of pesticides.
A group-contribution method for estimating the vapour pressure of organic compounds has been extended by Nannoolal et al. (2008). They defined many molecular groups and estimated their contribution to the slope of the vapour pressure - temperature curve (represented as $\log(P_{v,l})$ versus $1/T$). Moreover, they defined second-order groups, with the corresponding correction for the slope. Some functional groups were considered to be non-additive; showing interactions. Knowledge of a boiling point (measured or estimated) at a given pressure is required. It is advised to try using this extended method in future work on estimating the vapour pressure of pesticides.

Barley and McFiggans (2010) estimated the vapour pressure of organic chemicals in view of their partitioning between air and aerosols. First, they estimated the normal boiling points (T_b) using group contribution methods. The method of Nannoolal et al. (2004) provided the most accurate T_b values (as compared to measured values), while the method of Stein and Brown (1994) was the second best. After that, the vapour pressures were estimated by using the group contribution methods of Moller et al. (2008) and Nannoolal et al. (2008). The uncertainty in the estimated T_b values seemed to dominate the uncertainty in the vapour pressures.

First of all, the normal boiling point has to be estimated for many compounds, which means additional uncertainty when used in the estimation of vapour pressure (Barley and McFiggans, 2010). Especially extrapolation from high boiling points may be inaccurate.

Pesticides which are solid at environmental temperatures have two vapour pressures (Section 4.3): that of the solid state and that of the sub-cooled liquid state (Table 5.10). The difference between the two vapour pressures is higher as the melting point is higher. The ratio between the vapour pressure above the solid state of a compound and that above the sub-cooled liquid state at a certain temperature is indicated by Fugacity Ratio (Mackay et al. (2006a).

Table 5.10
Vapour pressures of the example pesticides at an environmental temperature in the solid (crystalline) and sub-cooled-liquid states (ChemSpider, 2010).

Pesticide	Melting point (K)	Vapour pressure (mPa) at 298 K in:	
		Solid state	Sub-cooled-liquid state
Chlorothalonil	523	0.076	12.8
Chlorpyrifos	315	2.71	3.99
Lindane	386	4.69	34.4
Pirimicarb	364	0.97	4.32
Quinoxyfen	380	0.020	0.13

The question rises which vapour pressure is most relevant in the different situations in the environment. In the first period after pesticide spraying, e.g. on plant surfaces, the deposit is wet/moist so the relatively strong crystalline interaction forces seem to be missing. After the deposit has dried, the pesticide is still mixed with substances from the formulated product sprayed. The interaction forces in the deposit could be lower than the pure-crystalline interaction forces. In the partitioning of pesticides over environmental compartments, the crystalline interaction forces do not seem to play a role. Various researchers point out that in estimating the distribution of compounds over environmental compartments, the vapour pressure (and solubility in water) for the sub-cooled liquid state should be used (Kühne et al., 1997; Goel et al., 2007; Barley and McFiggans, 2010).

6   Computed volatilisation of quinoxyfen from plants

6.1   Introduction

The fungicide quinoxyfen is an example of a pesticide with substantial uncertainty in its vapour pressure. Its vapour pressure is stated to be 0.012 mPa at 293 K in the EU list of endpoints (EC-DGHC, 2003; NL-Ctgb, 2005) and in Tomlin (2010). Unfortunately, the description of the method of determination/estimation of this vapour pressure is confidential company information. The company ascribes fungicidal vapour activity to the compound, which would be expected to occur at vapour pressures higher than that stated. Quinoxyfen was found to be somewhat volatile (15% of the dose) when sprayed on plants in a wind tunnel experiment (Wolters, 2003; Wolters et al., 2004). It may be difficult to explain such an extent of volatilisation on the basis of the very low vapour pressure stated.

Smit et al. (1998) derived an empirical relationship between the cumulative volatilisation from plants in seven days and the vapour pressure of the pesticides. Introduction of the vapour pressure of 0.012 mPa, stated for quinoxyfen, in their equation resulted in a calculated volatilisation of 4.3% of the dosage. It should be noted that the relationship of Smit et al. (1998) was based on only two points in the range of low to very low vapour pressures (0.01 to 0.1 mPa). There is an urgent need of more measurements on the volatilisation from plants for pesticides with low to very low vapour pressures.

To illustrate the problem of uncertainty in vapour pressure, some computations are carried out on the volatilisation of quinoxyfen from plants in a wind tunnel system (Wolters, 2003; Wolters et al., 2004). Quinoxyfen is a fungicide with protective action on the leaf surfaces, showing also some vapour action (Tomlin, 2003). The fungicide is stated to be translocated in the plants (systemic action). The vapour pressure of quinoxyfen is stated to be 0.012 mPa at 293 K (Tomlin, 2010; NL-Ctgb, 2005). Baloch et al. (1998b) passed an air flow from a cabinet with quinoxyfen-sprayed wheat plants to a cabinet with non-sprayed wheat plants. They measured effective vapour activity of quinoxyfen on fungal spores placed on the wheat plants in the downflow cabinet. Such a vapour activity would not be expected in the case of a very low vapour pressure. General input data for the computations on quinoxyfen could be taken from the simulation study of Leistra et al. (2008) on parathion-methyl, as the two pesticides were sprayed together on the wheat plants in the wind tunnel study. Specific input data on plant penetration and phototransformation of quinoxyfen have to be derived from a diversity of reported experimental data (as far as available).

6.2   Computations and input data

The computations on the volatilisation of quinoxyfen from plants were carried out with the PEARL model, as described for parathion-methyl by Leistra et al. (2008). Quinoxyfen and parathion-methyl were sprayed together on the wheat plants in the wind-tunnel experiment (Wolters, 2003; Wolters et al., 2004), which was simulated by Leistra et al. (2008). Consequently, some general input data can be adopted from the earlier simulation study for parathion-methyl. However, some specific input data for quinoxyfen have to be derived from a diversity of experimental results.

The computations are carried out with the PEARL model, in the same way as described for parathion-methyl by Leistra et al. (2008). The first three computations for quinoxyfen are carried out with a vapour pressure of 0.012 mPa at 293 K, as included in the EU list of endpoints (EC-DGHC, 2003), from confidential company information. Some estimation/calculation methods used in the present study (Section 5.7) indicate that the vapour pressure of quinoxyfen could be substantialy higher. Therefore, a vapour pressure of 0.10 mPa at 293 K was used in the fourth computation run.

The coefficient D_a for the diffusion of quinoxyfen in air was calculated with the FSG method, as described by Tucker & Nelken (1982). The value calculated for the reference temperature of 293 K is $D_a = 0.42$ m^2 d^{-1}.

In the wind tunnel experiment described by Wolters (2003) and Wolters et al. (2004), quinoxyfen was sprayed on the plants together with radiolabelled parathion-methyl. The processes for parathion-methyl in the wind tunnel system were simulated by Leistra et al. (2008). The value of the thickness of the laminar air boundary layer $d_{lam} = 0.35$ mm obtained for parathion-methyl should hold also for the volatilisation of quinoxyfen.

Unfortunately, the dosage of quinoxyfen in the experiment (corresponding to 0.0654 kg ha^{-1}) was low. Consequently, the accurate chemical analysis may have been more difficult than in the case of higher dosages. The fraction of the dosage of quinoxyfen intercepted by the plants (0.605) was set equal to that derived for parathion-methyl by Leistra et al. (2008).

Quinoxyfen is stated to be active through systemic acropetal and basipetal movement in the plants (Longhurst et al., 1996). However, Baloch et al. (1998b) found limited downward phloem mobility in wheat plants. Metabolism of quinoxyfen in wheat plants seems to proceed only gradually (Reeves et al., 1996). Phytotoxicity has been observed in cucurbits grown under cover (Tomlin, 2003).

On the basis of the scarce information on the penetration of quinoxyfen into plants, this penetration is classified to occur at moderate to low rate. Then the corresponding half-life of penetration proposed for computations (Leistra, 2005) is 3.0 d (rate coefficient $k_{pen} = 0.23$ d^{-1}).

The rate of phototransformation of quinoxyfen on the plants has to be estimated from a diversity of experimental data. The DT50 of photolysis in water was calculated to be 1.7 hours (June) to 22.8 hours (December) (Reeves et al., 1996; NL-Ctgb, 2005). Quinoxyfen is stated to be phototransformed on the wheat leaf surface, giving multiple polar transformation products (Reeves et al., 1996; Baloch et al., 1998a).

The residue of quinoxyfen applied to grapes and cucumbers grown under glass mainly consisted of quinoxyfen itself (Baloch et al., 1998a). This indicates that direct phototransformation predominantly occurs at the shorter wavelengths in the sunlight spectrum, which are filtered out by window glass of the glasshouses.

It should be noted that the wind tunnel used by Wolters et al. (1994) consisted of UV-transparent glass (side walls) and acrylic glass (lid). So the rate of pesticide phototransformation in their system was representative for outdoor conditions.

Soil photolysis is reported to be very slow (estimated $DT_{50,field} > 1$ year) (Reeves et al., 1996). The DT50 of photochemical oxidation in air is estimated by calculation to be 1.88 days (Reeves et al., 1996).

Quinoxyfen is stated to show long-term crop protection (up to 70 days) (Longhurst et al., 1996). This indicates that the rate of transformation on/in the plants only occurs at a low rate.

In summary, no quantitative data on the rate of phototransformation of quinoxyfen on plant surfaces are available. On the basis of the diversity of information, the phototransformation of quinoxyfen on plants is

estimated to occur at moderate to low rate. According to the classification of Leistra (2005), the corresponding half-life of phototransformation of 3.0 d ($k_{ph,ref}$ = 0.23 d^{-1}) at reference sunlight intensity (500 W m^{-2}) was used as a first approximation in computations.

The solubility of quinoxyfen in water is low: 0.116 mg L^{-1} (pH 6.45; 293 K) (Tomlin, 2010; NL-Ctgb, 2005). Log(Pow) for the octanol/water partitioning is reported to be 4.66 (pH 6.6; 293 K) (Tomlin, 2010; NL-Ctgb, 2005). The pKa value of protonated quinoxyfen is 3.56 (NL-Ctgb, 2005).

Quinoxyfen is stable to hydrolysis at pH 7 and pH 9 (dark; 298 K) (Reeves et al., 1996). At pH 4 to 5, a DT50 of 75 days (298 K) was measured for the hydrolysis (Reeves et al., 1996; NL-Ctgb, 2005).

Adsorption of quinoxyfen to soils is strong (Longhurst et al., 1996; Reeves et al., 1996). This can be expected to reduce its rate of volatilisation from soil. The rate of transformation of quinoxyfen in soils is low (Longhurst et al., 1996; Reeves et al., 1996).

The input data used in the computation runs, with their origin, are summarised in Table 6.1.

Table 6.1

*Input data for the computations on the volatilisation of quinoxyfen from wheat plants in a wind tunnel system.*

Quantity	Run	Value, unit	Reference
Molar mass	All runs	308.1 g/mol	Tomlin (2010)
Vapour pressure	Runs 1, 2 and 3	0.012 mPa at 293 K	EC-DGHC (2003); Tomlin (2010); NL-Ctgb (2005)
	Run 4	0.10 mPa at 293 K	High in range of estimates in the present report
Molar enthalpy of vaporisation	All runs	95 kJ mol^{-1}	Average of values for many pesticides (Smit et al., 1997)
Diffusion coefficient in air	All runs	0.42 m^2 d^{-1} at 293 K	Estimated by FSG method as described by Tucker and Nelken (1982)
Thickness laminar air boundary layer	All runs	0.35 mm	Derived by Leistra et al. (2008) for parathion-methyl in same system
Dosage	All runs	0.0654 kg ha^{-1}	Wolters (2003); Wolters et al. (2004)
Fraction intercepted by the plants	All runs	0.605	Derived by Leistra et al. (2008) for parathion-methyl
Rate coefficient for penetration into the plants	Runs 1 and 4	0.23 d^{-1}	Estimated in this study
Rate coefficient for phototransformation at reference sunlight	Runs 1 and 4	0.23 d^{-1}	Estimated in this study

6.3 Results

6.3.1 Measured course of volatilisation

The course of volatilisation in time measured for quinoxyfen in the wind tunnel experiment (Wolters, 2003; Wolters et al., 2004) is shown in Figure 2. There was no clear initial stage of comparatively fast volatilisation (as measured for parathion-methyl). Rather, volatilisation proceeded gradually over the whole experimental period. At two times (after two and eight days), there was a temporary increase in volatilisation rate, as compared to the period before. The increase in the volatilisation of quinoxyfen after eight days can be related to the sprinkler irrigation (8 mm) of the plants, both after seven and eight days. Possibly, some tightly-bound

deposit was released by the water and/or some poorly-exposed deposit was moved by the water to places in the canopy with a larger exposure to the air flow.
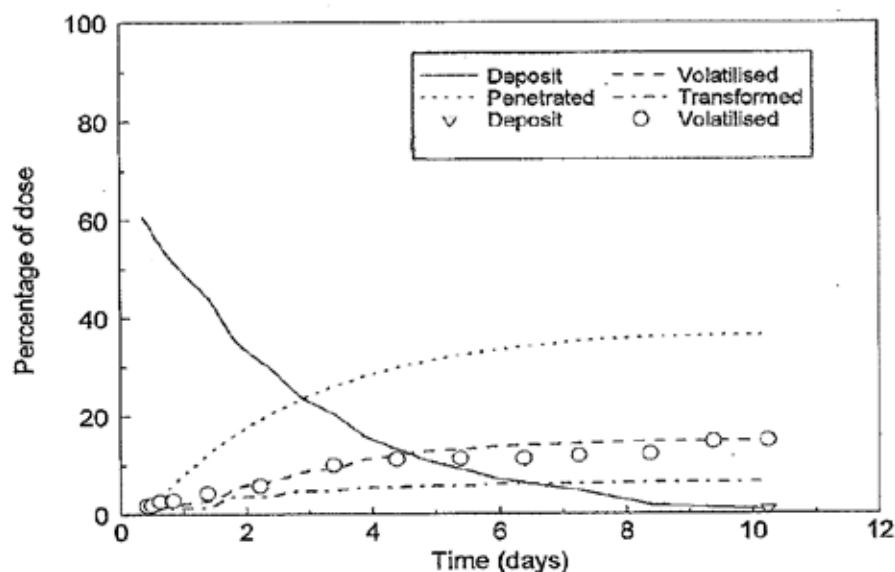
Figure 2

Measured (circles) and computed (dashed line) cumulative volatilisation of quinoxyfen from wheat plants in a wind tunnel. Results of computation Run 4. Computed deposit left on the plants (solid line), penetrated into the plants (dotted line) and phototransformed at the plant surface (dash-dot line).

6.3.2 Computed course of volatilisation

The first computation run (Run 1) on the volatilisation of quinoxyfen from the plants in the wind tunnel was carried out with the vapour pressure value of 0.012 mPa at 293 K, as given by EC-DGHC (2003) and NL-Ctgb (2005). The rate coefficient of penetration into the plants was set at k_{pen} = 0.23 d^{-1} ($t_{\frac{1}{2},pen}$ = 3 d). Similarly, the rate coefficient of phototransformation at reference sunlight radiation (500 W m^{-2}) was set at $k_{ph,ref}$ = 0.23 d^{-1} ($t_{\frac{1}{2},ph,ref}$ = 3 d). These values represent moderate to low rates for the processes (Leistra, 2005). Using these parameters, total volatilisation of quinoxyfen in the 10-day experimental period was computed to be 2.3 % of the dosage (measured: 15% of the dosage; Wolters et al., 2004).

In Run 2, the rate coefficient of penetration was lowered to 0.14 d^{-1} ($t_{\frac{1}{2},pen}$ = 5 d). The same lowered value was used for the rate coefficient of phototransformation : $k_{ph,ref}$ = 0.14 d^{-1} ($t_{\frac{1}{2},ph,ref}$ = 5 d). With these lowered values, the competing processes proceed slowly (Leistra, 2005). The lower competition by the two processes resulted in a cumulative volatilisation of quinoxyfen in the 10-day period of 3.3% of the dosage.

The final run for the lower vapour pressure (Run 3) was made with the low to very low values of k_{pen} = 0.07 d^{-1} ($t_{\frac{1}{2},pen}$ = 10 d) and $k_{ph,ref}$ = 0.07 d^{-1} ($t_{\frac{1}{2},ph,ref}$ = 10 d). Even with these low to very low rates of the competing processes, cumulative volatilisation was computed to be only 4.6% of the dosage. This is still distinctly lower than the measured volatilisation of 15% of the dosage.

The next run for quinoxyfen (Run 4) was made with the vapour pressure of 0.10 mPa at 293 K, which is high in the range of estimated values (Section 5.7). Penetration of quinoxyfen into the plants was simulated to occur at moderate to low rate: k_{pen} = 0.23 d^{-1} ($t_{\frac{1}{2},pen}$ = 3 d), just like phototransformation on the plants: $k_{ph,ref}$ = 0.23 d^{-1} ($t_{\frac{1}{2},ph,ref}$ = 3 d). Using these input values, cumulative volatilisation of quinoxyfen from the plants was computed to be 15.0% of the dosage. This corresponds to the measured total volatilisation.

The course of the volatilisation of quinoxyfen in time computed in Run 4 is shown in Figure 1, together with the measured cumulative volatilisation (Wolters, 2003; Wolters et al., 2004). Both computations and measurements show a gradual volatilisation in the course of the experimental period, up to 15% of the dosage at the end. The deposit on the plant surfaces only decreased at a moderate rate as a result of the three decline processes. The deposit computed to be left on the plants at the end of the study (0.9% of the dosage) corresponded to the measured water-rinsed deposit (also 0.9% of the dosage) (Wolters, 2003). Quinoxyfen penetration into the plants is simulated to be the most important process (36.8% of the dosage) acting upon the deposit. The sum of the amount of parent compound obtained by rinsing the plant surfaces with organic solvents at the end of the study was 10.0% of the dosage. The latter is only a fraction of the total plant-penetrated residue, which also includes the more deeply penetrated quinoxyfen and the transformation products. The presumably high percentage of penetration of quinoxyfen can explain its long-term protective action. The percentage phototransformed at the plant surfaces is simulated to be comparatively low (6.5% of the dosage). One of the factors is that sunlight irradation inside the wind tunnel was mostly much lower than the reference irradiation of 500 W/m^2. The use of non-labelled quinoxyfen in this study precludes a check on the computed material balance of the fungicide.

In summary, the gradual volatilisation of quinoxyfen from the plants in the wind tunnel can be explained with a vapour pressure of about 0.10 mPa at 293 K, in combination with moderate to low rates of the competing processes. The simulated plant penetration can explain the long-term fungicidal protection of the treated leaves, especially in combination with the presumably slow transformation in the plants.

A first requirement for a pesticide to be suitable for the development and testing of a volatilisation model is that its vapour pressure is known accurately. For that purpose, it should be possible to study and evaluate the quality of vapour pressure determination on the basis of a complete description of procedure and results.

Acknowledgement

Literature

Baloch, R., A.M.G. MacDonald, F. Pillar, C.Y. Caley and S. Chapleo, 1998a. *Degradation and metabolism of quinoxyfen in outdoor grown wheat, and indoor grown vines and cucumbers.* Abstract 5A-008. 9th Intern. Congress Pesticide Chemistry, 2-7 August 1998. London, UK.

Baloch, R., F. Geuguen, D. Bartlett and M. Greaves, 1998b. *Redistribution of quinoxyfen in a cereal crop.* Abstract 6E-006. 9th Intern. Congress Pesticide Chemistry, 2-7 August 1998. London, UK.

Balson, E.W., 1947. Studies in vapour pressure measurement. Part III. An effusion manometer sensitive to 5 x 10^{-6} millimetres of mercury: Vapour pressure of DDT and other slightly volatile substances. *Transactions Faraday Society* 43: 54-60.

Barley, M.H. and G. McFiggans, 2010. The critical assessment of vapour pressure estimation methods for use in modelling the formation of atmospheric organic aerosol. *Atmos. Chem. Phys.* 10: 749-767.

Baum, E.J., 1998. *Chemical property estimation: Theory and application.* Lewis Publishers, Boca Raton, FL, USA.

Bidleman, T.F., 1984. Estimation of vapor pressures for nonpolar organic compounds by capillary gas chromatography. *Anal. Chem.* 56: 2490-2496.

Boehncke, A., K. Martin, M.G. Müller and H.K. Cammenga, 1996. The vapor pressure of lindane (γ-1,2,3,4,5,6-hexachlorocyclohexane) – A comparison of Knudsen effusion measurements with data from other techniques. *J. Chem. Engin. Data* 41: 543-545.

Burkhard, L.P., A.W. Andren and D.E. Armstrong, 1985. Estimation of vapor pressures for polychlorinated biphenyls: A comparison of eleven predictive methods. *Environ. Sci. Technol.* 19: 500-507.

ChemSpider, 2010. Database of chemical structures and property predictions. www.chemspider.com

ChemStations Inc., 2009. CHEMCAD chemical process simulation software. www.chemstations.com

Constantinoui L. and R. Gani, 1994. New group contribution method for estimating properties of pure compounds. *Amer. Inst. Chem. Engin. J.* 40: 1697-1710.

Cordes, W. and J. Rarey, 2002. A new method for the estimation of the normal boiling point of non-electrolyte organic compounds. *Fluid Phase Equilibria 201*: 409-433.

Dearden, J.C., 2003. Quantitative structure-property relationships for prediction of boiling point, vapor pressure, and melting point. *Environ. Toxicol. Chem.* 22: 1696-1709.

Donovan, S.F.,1996. New method for estimating vapor pressure by the use of gas chromatography. *J. Chrom. A* 749: 123-129.

EC-DGHC, 2003. *Review report for the active substance quinoxyfen*. Report 6781/VI/97-Final. 27 November 2003. http://ec.europa.eu/food/plant/protection/evaluation/index_en.htm

EC-DGHC, 2005a. Review report for the active substance chlorpyrifos.
http://ec.europa.eu/food/plant/protection/evaluation/index_en.htm

EC-DGHC, 2005b. Review report for the active substance chlorpyrifos-methyl.
http://ec.europa.eu/food/plant/protection/evaluation/index_en.htm

EC-DGHC, 2006a. Review report for the active substance chlorothalonil.
http://ec.europa.eu/food/plant/protection/evaluation/index_en.htm

EC-DGHC, 2006b. Review report for the active substance pirimicarb.
EFSA Sci. Rep. 43: 1-76.

EC-DGHC, 2010. Database on active substances.
http://ec.europa.eu/sanco_pesticides/public/index.cfm

Emami, F.S., A. Vahid and J.R. Elliott, 2009. Finitely limited group contribution correlations for boiling temperatures. *J. Chem. Thermodynamics* 41: 530-537.

Giustini, A., B. Brunetti and V. Piacente, 1998. A sublimation study of lindane. *J. Chem Engin.* Data 43: 447-450.

Goel, A, L.L. McConnell and A. Torrents, 2007. Determination of vapor pressure –temperature relationships of current-use pesticides and transformation products. *J. Environ. Sci. Health* B42: 343-349.

Hilal, S.H., A.N. Saravanaraj, T. Whiteside and L.A. Carreira, 2007. Calculating physical properties of organic compounds for environmental modeling from chemical structure. *J. Comput. Aided Mol. Des.* 21: 693-708.

Hinckley, D.A., 1990. Determination of vapor pressures for nonpolar and semipolar organic compounds. *J. Chem Engin. Data* 35: 232-237.

Horvath, A.L., 1992. *Molecular design: Chemical structure generation from the properties of pure organic compounds.* Elsevier, Amsterdam, The Netherlands.

Jain, N. and S.H. Yalkowsky, 1999. *UPPER III: Unified physical property estimation relationships. Application to non-hydrogen bonding aromatic compounds. J. Pharmaceutical Sci.* 88: 852-860.

Joback, K.G. and R.C. Reid, 1987. *Estimations of pure-component properties from group-contributions. Chem. Engin. Commun.* 57: 233-243.

Joback, K.G., 2009. *Obtain the best physical property data. Chemical Engineering* Progress. *Amer. Inst. Chem. Engin.*, May 2009: 30-39.

Kim, Y.H, J.E. Woodrow and J.N. Seiber, 1984. *Evaluation of a gas chromatographic method for calculating vapor pressures with organophosphorus pesticides. J. Chrom.* 314: 37-53.

Kühne, R., R.U. Ebert and G. Schüürmann, 1997. Estimation of vapour pressures for hydrocarbons and halogenated hydrocarbons from chemical structure by a neural network. *Chemosphere* 34: 671-686.

Leistra, M., 2005. *Estimating input data for computations on the volatilisation of pesticides from plant canopies and competing processes.* Alterra-report 1256. Alterra, Wageningen University and Research Centre, Wageningen, The Netherlands.

Leistra, M., A. Wolters and F. van den Berg, 2008. Volatilisation and competing processes for a pesticide applied to plants in a wind tunnel system. *Pest Manag. Sci.* 64: 669-675.

Longhurst, C., K. Dixon, A. Mayr, U. Bernhard, K. Prince, J. Sellars, P.Prove, C. Richard, W. Arnold, B. Dreikorn and C. Carson, 1996. DE-795 – A novel fungicide for the control of powdery mildew in cereals. Brighton Crop Protection Conference – *Pests and Diseases*: 27-32.

Lyman, W.J., 2000. *Boiling point.* In: Handbook of property estimation methods for chemicals. Environmental and health sciences. Chapter 2. R.S. Boethling & D. Mackay (Eds). Lewis Publishers, Boca Raton FL, USA.

Mackay, D., A. Bobra, D.W. Chan and W.Y. Shiu, 1982. Vapor pressure correlations for low-volatility environmental chemials. *Environ. Sci. Technol.* 16: 645-649.

Mackay, D., W.Y. Shiu, K.C. Ma and S.C. Lee, 2006a. *Physical-chemical properties and environmental fate for organic chemicals* (2nd ed.). Vol I. Introduction and hydrocarbons. CRC Taylor & Francis, Boca Raton, FL, USA.

Mackay, D., W.Y. Shiu, K.C. Ma and S.C. Lee, 2006b. *Physical-chemical properties and environmental fate for organic chemicals* (2nd ed.). Vol IV. Nitrogen and sulfur containing compounds and pesticides. CRC Taylor & Francis, Boca Raton, FL, USA.

Marino , D.J., 2006. Variability in physical constant parameter values from standard data sources and the implication of this variability for risk analysis. *Risk Analysis* 26: 555-572.

Marrero-Morejon J. and E. Pardillo-Fontdevila, 1999. Estimation of pure compound properties using group-interaction contributions. *Amer. Inst. Chem. Engin. J.* 45: 615-621.

Mishra, D.S. and S.H. Yalkowsky, 1991. Estimation of vapor pressure of some organic compounds. *Ind. Engin. Chem. Res.* 30: 1609-1612.

Moller, B., J. Rarey and D. Ramjugernath, 2008. Estimation of the vapour pressure of non-electrolyte organic compounds via group contributions and group interactions. *J. Molecular Liquids* 143: 52-63

Myrdal, P.B. and S.H. Yalkowsky, 1997. Estimating pure component vapor pressures of complex organic molecules. *Ind. Engin. Chem. Res.* 36: 2494-2499.

Nannoolal, Y., J. Rarey, D. Ramjugernath and W. Cordes, 2004. Estimation of pure component properties. Part 1. Estimation of the normal boiling point of non-electrolyte organic compounds via group contributions and group interactions. *Fluid Phase Equilibria* 226: 45-63.

Nannoolal, Y., J. Rarey and D. Ramjugernath, 2008. Estimation of pure component properties. Part 3. Estimation of the vapor pressure of non-electrolyte organic compounds via group contributions and group interactions. *Fluid Phase Equilibria* 269: 117-133.

Neely, W.B. and G.E. Blau, 1976. The use of laboratory data to predict the distribution of chlorpyrifos in a fish pond. In: *Pesticides in aquatic environments*, p. 145. M.A.Q. Khan (ed.). Plenum Press, New York.

NL-Ctgb, 2001. *Chlorothalonil.* Pesticides database. Board for the Authorisation of Plant Protection Products and Biocides, Wageningen, The Netherlands.
www.ctgb.nl

NL-Ctgb, 2005. *Quinoxyfen.* Pesticides database. Board for the Authorisation of Plant Protection Products and Biocides, Wageningen, The Netherlands.
www.ctgb.nl

NL-Ctgb, 2009. *Chloorpyrifos.* Pesticides database. Board for the Authorisation of Plant Protection Products and Biocides, Wageningen, The Netherlands.
www.ctgb.nl

NL-Ctgb, 2010. *Pesticides database.* Board for the Authorisation of Plant Protection Products and Biocides, Wageningen, The Netherlands.
www.ctgb.nl

NL-RIVM, 1989. *Pirimicarb.* Adviesrapport 88/678801/110. National Institute of Public Health and the Environment, Bilthoven, The Netherlands.

NL-RIVM, 1992. *Lindaan.* Adviesrappport 91/678607/002. National Institute of Public Health and the Environment, Bilthoven, The Netherlands.

OECD, 1995. *Vapor pressure.* OECD Guideline for the testing of chemicals. Nr 104. Organisation for Economic Cooperation and Developement, Paris, France.

Pankow, J.F. and W.E. Asher, 2008. SIMPOL.1: a simple group contribution method for predicting vapor pressures and enthalpies of vaporization of multifunctional organic compounds. *Atmos. Chem. Phys.* 8: 2773-2796.

Racke, K.D., 1993. Environmental fate of chlorpyrifos. *Reviews Environ. Contam. Toxicol.* 131: 1-150.

Reeves, G.L., A.R. Gambie and R.I. Baloch, 1996. DE-795: *An environmental and exposure assessment.* Brighton Crop Protection Conference – Pests and Diseases: 1169-1174.

Reinhard, M. and A. Drefahl, 1999. *Handbook for estimating physicochemical properties of organic compounds.* John Wiley & Sons, New York, NY, USA.

Sanghvi, R. and S.H. Yalkowsky, 2006. Estimation of the normal boiling point of organic compounds. *Ind. Eng. Chem. Res.* 45: 2856-2861.

Simamora, P., A. Miller and S.H. Yalkowsky, 1993. Melting point and normal boiling correlations: Application to rigid aromatic compounds. *J. Chem. Inf. Comput. Sci.* 33: 437-440.

Simamora, P. and S.H. Yalkowsky, 1994. Group contribution methods for predicting the melting points and boiling points of aromatic compounds*. Ind. Eng. Chem. Res.* 33: 1405-1409.

Simmons, K.A., 1999. A simple structure-based calculator for estimating vapor pressure. *J. Agric. Food Chem.* 47: 1711-1716.

Smit, A.A.M.F.R., F. van den Berg and M. Leistra, 1997. *Estimation method for the volatilization of pesticides from fallow soil.* Environmental Planning Bureau Series 2, DLO Winand Staring Centre, Wageningen, The Netherlands.

Smit, A.A.M.F.R., M. Leistra and F. van den Berg 1998. *Estimation method for the volatilization of pesticides from plants.* Environmental Planning Bureau Series 4, DLO Winand Staring Centre, Wageningen, The Netherlands.

Spencer, W.F. and M.M. Cliath 1970. Vapor density and apparent vapor pressure of lindane (γBHC). *J. Agric. Food Chem.* 18: 529-530.

SRC, 2010. *SRC PhysProp Database*.
http://srcinc.com/what-we-do/environment.aspx

Staikova, M., P. Messih, Y.D. Lei, F. Wania and D.J. Donaldson, 2005. Prediction of subcooled vapor pressures of nonpolar organic compounds using a one-parameter QSPR. *J. Chem. Engin. Data* 50: 438-443.

Stein, S.E. and R.L Brown, 1994. Estimation of normal boiling points from group contributions. *J. Chem. Inf. Comput. Sci.* 34: 581-587.

Tomlin, C.D.S., 2003. *The pesticide manual.* A world compendium (13th ed.). British Crop Protection Council, Alton, Hampshire, UK.

Tomlin, C.D.S. (ed.), 2010. *The e-Pesticide Manual* (15th ed.). A World Compendium. British Crop Protection Council. BCPC Publications Sales, Alton, Hampshire, UK.

Tsuzuki, M., 2000. Thermodynamic estimation of vapor pressure for organo-phosphorus pesticides. *Environ. Toxicol. Chem.* 19: 1717-1726.

Tsuzuki, M., 2001. Thermodynamic estimation of vapor pressures for carbamate pesticides. *J. Pestic. Sci.* 26: 48-54.

Tucker, W.A. and L.N. Nelken, 1982. *Diffusion coefficients in air and water.* In: Handbook of chemical property estimation methods. Environmental behavior of organic compounds. W.J. Lyman, W.F. Reehl & D.H. Rosenblatt (eds). Chapter 17. McGraw-Hill Book Company, New York.

UN-WHO, 1991. Lindane. *Environmental Health Criteria* 124.
http://www.who.int

UN-WHO, 1996. Chlorothalonil. *Environmental Health Criteria* 183. http://www.who.int

UN-WHO, 2010. *Environmental Health Criteria (EHCs) published by the UN World Health Organisation in the framework of the International Programme on Chemical Safety (IPCS),* Geneva, Switzerland.
http://www.who.int/ipcs/publications/ehc/ehc_alphabetical/en/

US-EPA, 2001. *Lindane. Reregistration Eligibility Decision.*
http://www.epa.gov

US-EPA, 2002. *Chlorpyrifos. Reregistration Eligibility Decision*. http://www.epa.gov

US-EPA, 2004. *Estimation Programs Interface, EPI Suite, version 3.12.* Exposure Assessment Tools and Models. US Environmental Protection Agency, Washington DC, USA. www.epa.gov/oppt/exposure/docs/episuitedl.htm

US-EPA, 2010. *Peer Reviews of the US Environmental Protection Agency.* Washington DC, USA. http://www.epa.gov/pesticides

Walters, A.E., P.B. Myrdal and S.H. Yalkowsky, 1995. A method for estimating the boiling points of organic compounds from their melting points. *Chemosphere* 31: 3001-3008.

Wania, F., W.Y. Shiu and D. Mackay, 1994. Measurement of the vapor pressure of several low-volatility organochlorine chemicals at low temperatures with a gas saturation method. *J. Chem. Eng. Data* 39: 572-577.

Waser, J., 1966. *Basic chemical thermodynamics.* W.A. Benjamin, New York, USA.

Wolters, A., 2003. *Pesticide volatilization from soil and plant surfaces: Measurements at different scales versus model predictions.* Dissertation, University of Aachen. Berichte des Forschungszentrums Jülich4073, Jülich, Germany.

Wolters, A., M. Leistra, V. Linnemann, M. Klein, A. Schäffer and H. Vereecken, 2004. Pesticide volatilization from plants: Improvement of the PEC model PELMO based on a boundary layer concept. *Environ. Sci. Technol.* 38: 2885-2893.

Xiao, H., N. Li and F. Wania, 2004. Compilation, evaluation and selection of physico-chemical property data for α, β, and γ hexachlorocyclohexane. *J. Chem. Engin. Data* 49: 173-185.

Yalkowsky, S.H., J.F. Kryzaniak and P.B. Myrdal, 1994. Relationships between melting point and boiling point of organic compounds. *Ind. Eng. Chem. Res.* 33: 1872-1877.

Appendix I Description of quantities, expressions and acronyms

(simplified in various cases)

Boiling point equation: At the boiling point, the free energy of transition is zero so T_b = (molar enthalpy of boiling ΔH_b)/(molar entropy of boiling ΔS_b) (e.g. Sanghvi and Yalkowski, 2006).

CAS number: Chemical Abstracts Service Registry Number. Unique number for chemical compounds often used in software packages.

Descriptors: description parameters related to the structure of the molecule and the interactions between atoms and groups.

Descriptor types (examples):
– topological: parameters describing the structural arrangement of the atoms/groups in the molecule;
– topochemical: parameters describing the structural arrangement and chemical interactions of atoms/groups in the molecule;
– electrotopological: parameters describing the structural arrangement and electronic interactions of the atoms/groups in the molecule.

Enthalpy: the enthalpy of boiling is the amount of energy required to vaporise 1 mol of a compound at its boiling point (e.g. Sanghvi and Yalkowski, 2006). Unit: J mol^{-1}.

Entropy: the entropy of boiling is a measure of the increase in randomness of a system upon boiling (e.g. Sanghvi and Yalkowski, 2006). Unit J mol^{-1} K^{-1}.

EPI: Estimation Program Interface.

EPI Suite: Suite of physical/chemical property and environmental fate estimation programs, developed by US-EPA and Syracuse Research.

External rotational symmetry number of the molecule: number of identical images that can be produced by rigid rotation of the molecule.

Flexibility: ability of the atoms in molecules to torsionally rotate about single bonds.

Fugacity Ratio: ratio between the vapour pressures of a substance above its solid state and its sub-cooled liquid state at a certain temperature.

Molecular flexibility number: the number of reasonable conformations in which the molecule can exist (Mishra and Yalkowski; 1991).

Parachor: molecular mass of a liquid times the fourth root of its surface trension, divided by the density.

QSPR = Quantitative Structure-Property Relationship.

Rotational symmetry number: the number of ways that the molecule can be positioned that are identical to a reference position (Mishra and Yalkowsky, 1991).

SMILES = Simplified Molecular Input Line Entry System. Notation system often used for introducing molecular structures in software packages.

Troutons rule: the molar entropy of boiling ΔS_b of many organic compounds is roughly constant at 88 J mol^{-1} K^{-1}. The rule holds for rigid organic compounds without hydrogen bonds.

UNIFAC: UNIversal Functional Activity Coefficient. UNIFAC is a method for the estimation of activity coefficients of compounds in solution, based on a group contribution methodology.

UPPER: Unified Physical Property Estimation Relationships.
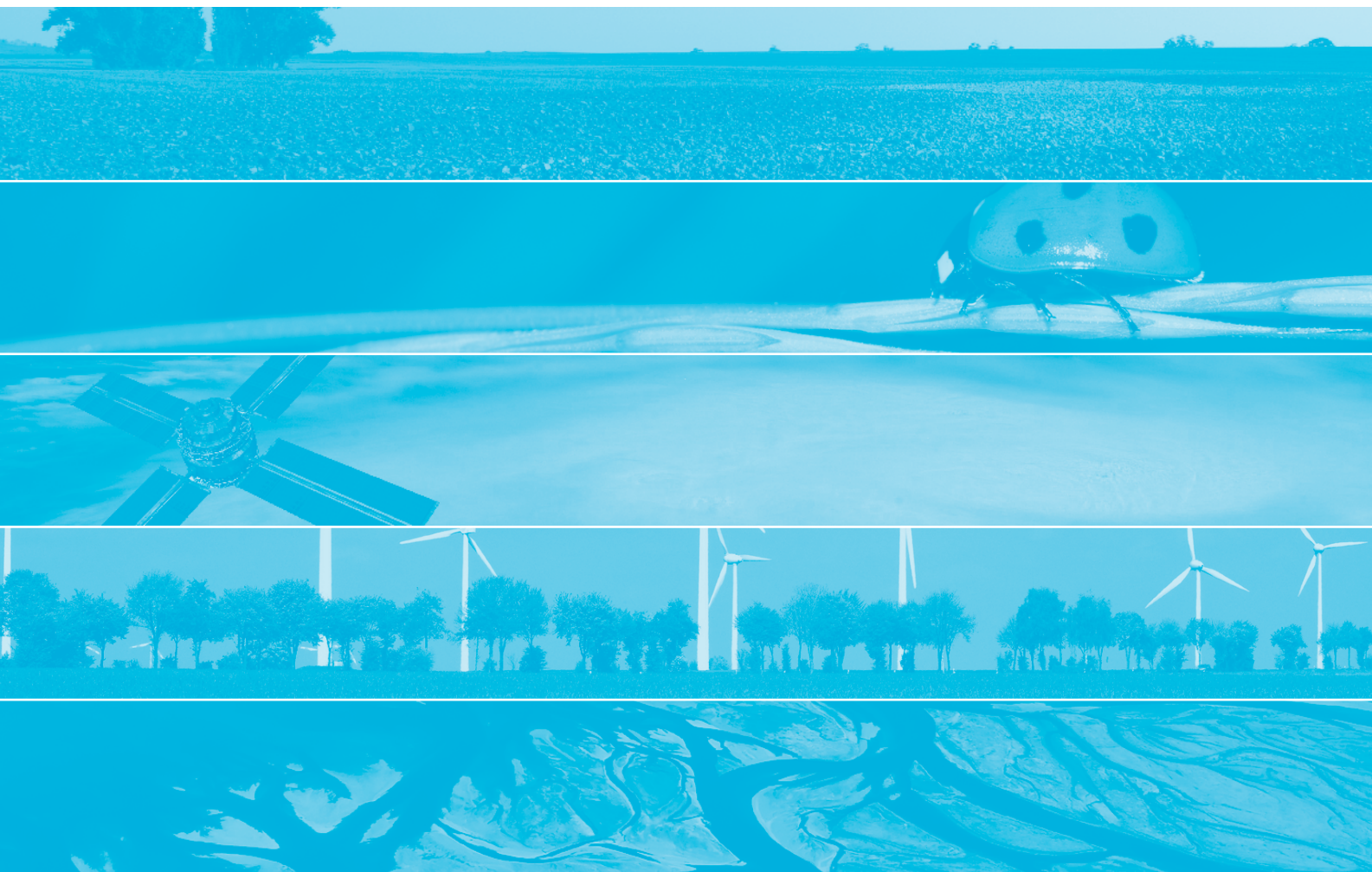
Alterra is part of the international expertise organisation Wageningen UR (University & Research centre). Our mission is 'To explore the potential of nature to improve the quality of life'. Within Wageningen UR, nine research institutes – both specialised and applied – have joined forces with Wageningen University and Van Hall Larenstein University of Applied Sciences to help answer the most important questions in the domain of healthy food and living environment. With approximately 40 locations (in the Netherlands, Brazil and China), 6,500 members of staff and 10,000 students, Wageningen UR is one of the leading organisations in its domain worldwide. The integral approach to problems and the cooperation between the exact sciences and the technological and social disciplines are at the heart of the Wageningen Approach.

Alterra is the research institute for our green living environment. We offer a combination of practical and scientific research in a multitude of disciplines related to the green world around us and the sustainable use of our living environment, such as flora and fauna, soil, water, the environment, geo-information and remote sensing, landscape and spatial planning, man and society.

More information: www.alterra.wur.nl/uk