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Summary

All references to energy for pesticide production in agriculture can be traced back to the original data of Green (1987). The most common method used to derive values for current chemicals is to use the average of each category of active ingredient. However a comparison of the mean and standard deviation of the categories provides little justification for using anything other than the overall average for agrochemicals, both for the total energy used and the breakdown into the different sources of inherent and process energy. However it is likely that using energy requirements derived directly from Green, such as the mean or maximum will generally underestimate for chemicals introduced since 1985.

Of the methods tested to derive improved estimates, the only practical and effective one is to use a linear regression on the year of discovery. From these data, the total pesticide energy input to each type of crop by category of pesticides can be calculated. This is 1681 MJ/ha for wheat. It seems reasonable that 1130 is a minimum and 3280 is a maximum value for wheat.

Table 1 lists the appropriate values for each crop per hectare and the weighted average pesticide production energies per unit mass of the different types of pesticide – overall 370 MJ/kg active ingredient.

Table 1. Standard pesticide energy input to arable crops, MJ per hectare

	Fungicide	Herbicide	Insecticide	Molluscide	Growth regulator	Seed treatment	TOTAL
Wheat	475	792	28	11	340	35	**1681**
Winter barley	301	802	10	2	230	15	**1359**
Spring barley	254	225	6	0	18	14	**516**
Oats	130	154	6	0	201	21	**512**
Rye	85	1005	11	2	97	20	**1220**
Triticale	63	248	3	0	36	7	**357**
Oilseed rape	188	752	17	29	0	15	**1001**
Linseed	42	756	4	0	0	132	**934**
Potatoes	2912	896	751	37	132	154	**4883**
Peas	330	979	31	0	0	60	**1401**
Beans	363	645	15	1	0	0	**1025**
Sugar beet	66	2283	18	1	0	300	**2667**
Set-aside	32	395	3	5	1	4	**439**
Forage Maize	0	540	4	1	0	27	**571**
Weighted average	**396**	**706**	**41**	**10**	**175**	**36**	**1364**
Weighted average pesticide production energy, MJ/kg ai							
	423	**386**	**274**	**154**	**276**	**511**	**370**

A factor of 0.069 kg CO_2 equivalent per MJ pesticide energy can be used to convert these to the Global Warming Potential (100 years). The pesticide energy input of 1364 MJ/ha thus corresponds to a weighted average greenhouse gas emission of 94 kg CO_2 equivalent per hectare of arable crop.

The results show that pesticide manufacturing represents about 9% of the energy use of arable crops – less for spring crops and more for potatoes. The amount represents about 100-200 MJ/t of crop. Given the above maxima and minima, the range is no lower than 6% and no higher than 16%.

Pesticide manufacturing represents about 3% of the 100-year Global Warming Potential (GWP) from crops. This lower value is because about 50% of the GWP from arable crops is due to the field emissions of nitrous oxide from the soil which has a very large GWP.

The above values come with a very wide range of uncertainty. There would thus be considerable benefit to more detailed information on the energy required for the manufacture of some current pesticides. This may be possible by repeating the method of analysis of Green using patent data on modern pesticides, in conjunction with an industrial organic chemist, but actual plant data would be preferable. Indeed the latter is essential for use in a procedure for "carbon footprinting", such as that being sponsored by the Carbon Trust and Defra in the BSI's Publicly Available Specification PAS2050. Corporate Environmental data published by Monsanto suggest that energy consumption in their chemical plants may have reduced by up to 47% in the last 20 years.

1. Introduction

With the rapidly growing interest in greenhouse gas emissions (often embodied in Life Cycle Assessment or "carbon footprinting"), there are many studies using estimates of the emissions from agricultural pesticide manufacturing. Unfortunately, it seems that almost no two studies use the same number for the same ingredient. This is mainly due to the paucity of original data on pesticides, often because of commercial confidentiality. There is also a wide range of energy used in producing different pesticides and significant changes over the years in the pesticide ingredients used.

There is a need for the agricultural pesticide industry to produce a (set of) reliable number(s) that can be used uniformly in discussions about greenhouse gas emissions and pesticides. Given that these emissions are intimately associated with energy consumption, this needs to be standardised too.

Cranfield University was asked by the Crop Protection Association to carry out a study of the major agricultural pesticides for manufacturers to produce an up-to-date (set of) reliable number(s) for the greenhouse gas emissions (quantified as Global Warming Potential, GWP, with units of CO_2 equivalent, CO_2e) and energy consumption from pesticide manufacturing per kg active ingredient, and hence to determine estimates of CO_2e emissions from agricultural pesticide manufacturing per unit area. This study was to be based on existing literature only and not an analysis of actual energy use and processes used by current pesticide manufacturers.

2. The literature

The most well established source of information on pesticide manufacturing energy is Green (1987), whose numbers are recorded in Table 2. Only a few of these pesticides are still used. These were derived from constructed material flow sheets derived from information about the method of manufacture in the patents. *Process energy* is the energy required in the manufacturing process to produce the chemicals such as heating, creating pressure and cooling, plus the energy needed to create and transmit that energy to the manufacturing

process. For electricity, this is typically of the order of three times the measured electricity use on site. *Inherent energy* is the primary energy resource used in the production of the chemical but retained in the chemical structure of the pesticide.

Green states that the estimates for older pesticides no longer under patent protection are probably of the order of ±10%, but others are the 'order of energy contents' and are at best approximate. He notes that companies strive to reduce the energy required. Green derived and used these data in earlier work comparing systems of agricultural production using more or less amounts of herbicides such as Green (1976) and Green & McCulloch (1976).

Table 2. Energy requirements for production of pesticides in MJ/kg active ingredient (ai), from Green (1987)

			Total inherent energy†			Total process energy*			Total
Active ingredient		**Chemical family[1]**	**Naphtha**	**Gas**	**Coke**	**Fuel oil**	**Electricity**	**Steam**	**Energy**
MCPA	H	Phenoxy	53.3	12.0	0.0	12.6	27.5	22.3	127.7
2,4-D	H	Phenoxy	39.0	0.0	0.0	9.0	23.0	16.0	87.0
2,4,5-T	H	Phenoxy	43.0	23.0	0.0	2.0	42.0	25.0	135.0
Dicamba	H	Benzoic	69.0	73.0	0.0	4.0	96.0	53.0	295.0
Chloramben	H	Benzoic	92.0	29.0	0.0	5.0	44.0	0.0	170.0
Fluazifop-butyl	H	phenoxy, trifluoromethyl, pyridine	89.2	71.6	0.0	8.6	183.4	165.2	518.0
Propanil	H	Acetamide	62.0	40.0	0.0	3.0	64.0	51.0	220.0
Alachlor	H	Acetamide	98.6	27.8	0.0	12.1	86.4	52.6	277.5
Propachlor	H	Acetamide	107.0	29.0	0.0	14.0	84.0	56.0	290.0
Chlorsulfuron	H	urea, triazine	91.3	35.6	0.0	7.8	112.2	118.5	365.4
Butylate	H	Thiocarbamate	42.1	33.2	11.6	6.8	31.0	16.1	140.8
Diuron	H	Urea	92.3	63.1	0.0	5.2	85.6	28.3	274.5
Fluometuron	H	urea, trifluoromethyl	118.6	72.1	0.0	8.7	98.5	56.7	354.6
Atrazine	H	Triazine	43.2	68.8	0.0	14.4	37.2	24.7	188.3
Dinoseb	H	Nitro compound	49.0	9.0	0.0	11.0	3.0	8.0	80.0
Trifluralin	H	trifluoromethyl, dinitroaniline	56.4	12.8	0.0	7.9	57.7	16.1	150.9
Diquat	H	Bipyridylium	70.0	65.0	0.0	1.0	100.0	164.0	400.0
Paraquat	H	Bipyridylium	76.1	68.4	0.0	4.0	141.6	169.3	459.4
Glyphosate	H	Organophosphonate	33.0	93.0	0.0	1.0	227.0	100.0	454.0
Linuron	H	Urea	96.5	68.1	0.0	6.6	88.4	30.1	289.7
Cyanazine	H	Triazine	54.6	65.8	0.0	15.2	38.6	26.8	201.0
Bentazon	H	Benzothiadiazole	128.6	66.1	0.0	42.3	118.5	78.1	433.6
EPTC	H	Carbamate	16.5	39.6	0.0	8.9	66.7	28.1	159.8
Metolachlor	H	Acetamide	101.2	27.6	0.0	15.1	78.2	53.7	275.8
		Average	**71.8**	**45.6**	**0.5**	**9.4**	**80.6**	**56.7**	**264.5**
		Standard deviation	**29.5**	**25.6**	**2.4**	**8.3**	**51.6**	**50.7**	**126.3**
Ferbam	F	dithiocarbamate, organoiron	0.0	42.0	3.0	0.0	13.0	23.0	81.0
Maneb	F	dithiocarbamate, organomanganese	27.0	23.0	8.0	9.0	25.0	7.0	99.0
Captan	F	Phthalimide	38.0	14.0	0.0	0.0	52.0	11.0	115.0
Benomyl	F	benzimidazole, MBC	86.7	71.2	0.0	14.3	121.2	103.6	397.0
		Average	**37.9**	**37.6**	**2.8**	**5.8**	**52.8**	**36.2**	**173.0**
		Standard deviation	**36.2**	**25.3**	**3.8**	**7.1**	**48.4**	**45.5**	**150.0**
Methyl parathion	I	organophosphorus, nitro compound	37.0	24.0	6.0	2.0	73.0	18.0	160.0
Phorate	I	Organophosphorus	56.1	34.2	0.0	5.6	89.5	23.6	209.0
Carbofuran	I	Carbamate	137.0	63.0	1.0	44.0	127.0	82.0	454.0
Carbaryl	I	Carbamate	11.0	48.0	26.0	1.0	54.0	13.0	153.0
Toxaphene	I	Organochlorine	3.0	19.0	0.0	1.0	32.0	3.0	58.0
Cypermethrin	I	Pyrethroid	89.0	71.2	0.0	10.3	199.5	210.0	580.0
Chlordimeform	I	Formamidine	61.8	53.1	0.0	6.5	86.5	42.3	250.2
Lindane	I	Organochlorine	6.2	16.3	0.0	2.2	30.6	2.5	57.8
Malathion	I	Organophosphorus	62.0	41.2	0.0	6.1	92.1	27.4	228.8
Parathion	I	organophosphorus, nitro compound	35.0	23.1	5.2	1.6	57.1	16.0	138.0
Methoxychlor	I	organochlorine, bridged diphenyl	10.2	11.6	0.0	2.4	28.7	16.9	69.8
		Average	**46.2**	**36.8**	**3.5**	**7.5**	**79.1**	**41.3**	**214.4**
		Standard deviation	**41.1**	**20.0**	**7.8**	**12.5**	**50.4**	**60.1**	**165.8**

1. Hartley D. and H.Kidd (1987)
2. H herbicide, F fungicide, G growth regulator, I insecticide

† Energy retained in the chemical structure of each pesticide

* Energy used in providing heat etc.

Pimentel (1980, p 45) quotes Green (1976) data, Table 3. Those data which claim to be from Green, are largely the same with some differences. There are three additions, for example for 2,4-D (a 'personal observation'). Unlike Green (1987) who quotes 20, 30, 20 MJ/kg ai for oil,

powder and granules formulations, and 3 MJ /kg ai for packaging and transport, Pimental quotes 180, 24, 184 MJ/kg ai for formulation, packaging and transport.

Table 3. Energy requirements for pesticides (MJ/kg ai) as reported from Green (1976) by Pimental (1980)

Active ingredient	Green 1987	Pimental 1980 from Green 1976	
MCPA	127.7	130	
2,4-D	87.0	101	Personal observation
2,4,5-T	135.0	237	
Dicamba	295.0	294	
Chloramben	170.0	299	
Propanil	220.0	219	
Propachlor	290.0	289	
Diuron	274.5	269	
Atrazine	188.3	189	
Dinoseb	80.0	80	
Trifluralin	150.9	147	
Diquat	400.0	399	
DDT		101	Leech & Slesser, 1973
Paraquat	459.4	459	
Glyphosate	454.0	453	
Ferbam	81.0	64	
Maneb	99.0	99	
Captan	115.0	115	
Methyl parathion	160.0	58	
Carbofuran	454.0	453	
Carbaryl	153.0	153	
Toxaphene	58.0	160	
Methyl bromide		67	Personal observation

Table 4. Energy requirements for production of pesticides applied to wheat, current at that time, estimated by Audsley *et al* (1997), MJ/kg ai

		Total inherent energy			Total process energy		Total
		Naphtha	Natural gas	Coke	Fuel oil	Electricity	energy
Carbendazim	F	86.7	71.2	0	117.9	124.2	400
Chlorothalonil	F	38	14	0	11	55	118
Cyproconazole	F	37.9	37.6	2.8	42	55.8	176
Fenpiclonil	F	37.9	37.6	2.8	42	55.8	176
Fenpropidin	F	37.9	37.6	2.8	42	55.8	176
Flusilazole	F	37.9	37.9	2.8	42	55.8	176
Hexaconazole	F	37.9	37.6	2.8	42	55.8	176
Tebuconazole	F	37.9	37.6	2.8	42	55.8	176
Chlormequat	G	61.1	42.3	1.6	58.7	80.3	244
Ethephon	G	61.1	42.3	1.6	58.7	80.3	244
Mepiquat chloride	G	61.1	42.3	1.6	58.7	80.3	244
Trinexapac-ethyl	G	61.1	42.3	1.6	58.7	80.3	244
Diflufenican	H	88.1	52.2	0	87.7	116.2	344.2
Fluroxypyr	H	71.8	45.6	0.5	66.1	83.6	267.5
Ioxynil	H	71.8	45.6	0.5	66.1	83.6	267.5
Isoproturon	H	99.7	59.7	0	65.5	99.2	324.1
Mecoprop-P	H	56.1	26.7	0	65.2	72	219.9
Cypermethrin	I	89	71.2	0	220.3	202.5	583
Pirimicarb	I	54.8	50.2	9	59	85.6	258.6
Methiocarb	S	54.8	50.2	9	59	85.6	258.6

The Green 1987 data were used in the EU Harmonisation study (Audsley *et al*, 1997) as the basis for deriving the values for pesticides current at that time and used on wheat. The procedure used was to determine its chemical family using the chemical classification proposed by Hartley and Kidd (1987). If the active ingredients listed by Green (1987) belonged to the same chemical family, then their average energy requirement was attributed to the new active ingredient. If no active ingredient listed by Green (1987) belonged to the chemical family of the new active ingredient, the average energy requirement was based on the type of pesticide. This produced Table 4 for the pesticides applied to wheat, current at that time. They also examined other emissions from pesticide production and concluded they can be regarded as negligible and omitted from an analysis.

Barber (2004) quotes energy per unit of active ingredient using categories of pesticides, which are stated as adapted from Pimentel (1980) having removed the formulations that have been withdrawn from the market. Energy for formulating, packaging and transportation which adds approximately a further 110 MJ/kg ai, is similar to Pimental's figures, Table 5. Lillywhite (2007) also uses categories but derives different numbers, which are consistent with being the average of Green (1987). The most commonly cited Life Cycle Inventory (LCI) database, Ecoinvent, also refers back to Green's data.

Table 5. Energy input for agrochemical categories from Barber (2004) and Lillywhite (2007)

		Barber (2004)		Lillywhite (2007)
Herbicide	**Production**	**Formulation, packaging and transport**	**Total MJ/kg ai**	**Total MJ/kg ai**
Preglone & Glyphosate	440	110	550	454
Not Preglone & Glyphosate	200	110	310	264
General	320	110	430	
Insecticide	185	126	310	214
Fungicide	97	113	210	168

There are numerous other studies using pesticide energy per hectare of crop production. Many only use a single figure, but for example Helsel (1993) quotes a list of specific pesticides in BTUs/lb. On inspection they are a subset of Green and on conversion to MJ are identical. (Helsel was the editor of the book containing Green's 1987 paper.) Milà i Canals (2006) uses the approach from Audsley (1997) based on Green (1987). Bailey *et al* (2003) used Green (1987) and averages for other pesticides. Lal (2004) also uses the data from Green, via Helsel and West and Morland (2002) via Pimentel.

A Congressional Research Service (CRS) report estimates that pesticides accounted for 6.3% of the energy used in agriculture in the USA in 2002. Estimates by ADAS for Defra's Sustainable Farming and Food Strategy (SFFS) suggest that 8% of energy used is for pesticide production.

Monsanto in their 2007 Pledge report quote that their products from their chemical plants in the USA use 48.5 GJ/t of energy consumption and emit 3.23 t CO_2e/t of direct greenhouse gas emissions. The methodology used only reports actual energy purchased. Thus the primary energy to produce electricity which amounts to one third of their energy consumption would need to be added. In addition the energy required to produce any other non-energy raw materials which have been purchased is omitted. However the main problem

is that there is no breakdown of how the energy relates to the different products, which range from chemicals to seeds, or even which of their products are covered by the analysis. Thus 400,000t of seeds requiring 40 MJ/kg and 4000t of chemical requiring 900 MJ/kg would produce the above result. (The output is quoted as 404,000t) Glyphosate as calculated by Green is 296 MJ direct energy/kg if manufactured entirely on site. Monsanto report that since 1990, for a comparable product mix, output has increased by 231,000 t and the energy used has reduced by 42.8 GJ/t. This would imply a reduction in Green's analysis for glyphosate from 454 MJ/kg to 241 MJ/kg, a reduction of 53%, but it is not clear whether or to what extent such a saving in total energy can be realised in any pesticides, including glyphosate. However gradual process optimisation over time is very likely to be reducing energy required.

Alternative derivations

Geisler (2004) has attempted to get around the problem of no recent inventory data for chemicals by developing a procedure for the systematic estimation of mass and energy flows (Life-Cycle Inventory, LCI) for the production of active substances and their precursors. Dahllöf (2007) adopted a statistical approach based on factors such as carbon bonds and number of reaction steps. However they did not find a significant improvement in estimating the process flows from the production of chemicals, compared with the method of grouping.

Summary

All references to energy for pesticide production in agriculture can be traced back to Green's original data. The most common method used to derive values for current chemicals is to use the average of each category of active ingredient. However a comparison of the mean and standard deviation of the categories (Table 2) provides little justification for using anything other than the overall average for agrochemicals, both for the total energy used and the breakdown into the different sources of inherent and process energy.

More recently there have been attempts to find a way to estimate chemical production process energies, but with no apparent success.

Greenhouse gas emissions

It is clear that the emissions from pesticide production apart from energy use can be ignored as contributors to Global Warming Potential (GWP) and therefore it is only necessary to determine the primary energy use. Audsley (1997) calculated the energy carriers used in the manufacture of the pesticides using the data supplied by Green. The GWP 100 emissions from these energy carriers were derived in Williams (2006). This concludes that a value of 0.069 kg CO_2e per MJ can be used to convert primary energy. Where electricity is used, then if electricity is all generated using hydro or nuclear power, and emitting very little carbon, then this factor becomes 0.049. (In fact the primary energy input becomes lower and the conversion factor remains similar) As an example the UK generates typically one third of its electricity from hydro and nuclear power compared to a half in Europe.

It is assumed that in due course all the carbon included in the pesticide will be broken down and emitted to the atmosphere as carbon dioxide. It is reasonable to assume other breakdown products are not highly active gases (such as nitrous oxide) and a worst case analysis suggests that, even if they were, then it would increase GWP by at most 1%.

3. Estimating pesticide energy requirements

It is agreed that the energy required to produce pesticides per unit ai, has increased over the years (van Laak, personal communication) as they have become more complex. At the same time, the weight of pesticide required per hectare has generally decreased, due to the increased activity per unit of chemical, so that it is not necessarily the case that overall pesticide energy per hectare for a chemical has increased. The above procedures using averages of categories from Green's data, will therefore tend to under estimate the energy requirement of modern products. The following questions were thus raised and are answered in the subsequent sections.

- Have prices increased with the recent oil prices surges?
- Does energy depend on process steps?
- Is it possible to use characteristics of the chemicals such as molecular structure?
- Is energy per year of discovery a better predictor?
- Is energy per hectare a more plausible categorisation?

3.1 Hypothesis: price change reflects energy requirement

With the substantial sharp increases in the price of oil ($25 to $50 and most recently $50 to over $100 per barrel), costs of energy for pesticide production have increased and these ought to be reflected in the prices – particularly of older chemicals. The change in the price of fertiliser is clearly related to energy prices (Elliott *et al*, 2007). Pesticide price changes were therefore analysed for similar patterns that could be used to indicate the energy requirement.

Estimates of market prices (£/l) for pesticides were extracted from Farm Brief (Lakebourne Farmbrief Limited, Holt) issues published between March and June in 1997, 2000 and 2003–2008. Common branded and generic products were used, including 9 herbicides, 6 fungicides and 6 insecticides. Data were not available for all pesticides every year. In particular, several products first appeared in the list in 2000, and several herbicides were withdrawn between 2007 and 2008. Where prices were available for a generic and a branded product with the same active ingredient, the one with the most complete set of prices was chosen.

An average price index for each group was calculated using 2007 as a base, because it had the most complete set of prices (Table 6). Glyphosate was removed from the index for 2008, because its prices has increased by a factor of 2.5, which has been attributed to factors other than energy prices, including shortage of supply from the principal manufacturer and increased demand following the withdrawal of paraquat in the EU and the introduction of "Roundup Ready" crops in some countries.

Table 6. Average pesticide price indices

Year	1997	2000	2003	2004	2005	2006	2007	2008
Oil price[1]	0.33	0.39	0.44	0.50	0.72	0.98	1.00	1.50
Herbicides	1.72	1.08	0.96	0.95	0.99	0.99	1.00	0.99
Fungicides	1.52	0.99	0.97	1.00	1.00	1.03	1.00	1.02
Insecticides	1.62	1.06	0.99	0.99	1.02	1.05	1.00	1.14

[1] Average of 12 months to June of three spot prices: Dated Brent, West Texas Intermediate, and the Dubai Fateh, based on data from IMF.

The decrease in price between 1997 and 2000 occurred despite increases in energy prices; it may be related to the fall in grain prices in the same period. The indices from 2000 onwards

do not show a clear trend related to energy prices. The increase in the index for insecticides in 2008 is due to one chemical, cypermethrin, increasing from £3/l to £5/l. If this is removed, the index for 2008 is 1.03.

Closer examination of the prices of individual products showed slight differences in behaviour between the cheaper, usually generic, products and the more expensive, usually branded, products. Several older products, with prices below £5/l increased by £0.4–1.9/l. The majority of products over £10/l remained stable, but some of the products introduced in the late 1990s, such as strobilurin fungicides showed modest price falls from 2000 onwards.

The energy requirements for the products from Green (1987) for which current prices were found, with the exception of glyphosate, was 60–100 MJ/l, based on the active ingredient only. This is equivalent to a cost of £0.5–0.84 per litre at £0.0084/MJ ($100/barrel). These products were among the group showing price increases, so it is plausible to assume that the increases were partly due to the change in energy prices. The stability of the prices of other products implies that energy is a smaller proportion of the cost, so the energy requirement is probably of the same order of magnitude as for the older chemicals and does not exceed 1000 MJ/kg. Glyphosate was an exception. If Green's value of 454 MJ/kg is correct, that equates to £0.70/l at £0.0042/MJ (*c* 2004), compared with a price in 2007 of £1.60/l. There is insufficient information to be sure whether this is correct, but acceptable due to the scale of production, a change in efficiency, or an error in Green.

Hypothesis: energy requirement depends on process steps

The estimates by Green (1987) included an assessment of the process steps used in the production of the chemicals considered. This information is not readily available for the majority of pesticides now in use, although production of a few of the older ones is described in publicly accessible sources (see Table 7). A minority of the entries in Tomlin (2003) include patent numbers. Where patents can be found, they often describe the laboratory preparation of groups of chemicals, not industrial production of specific ones (see Figure 1). Interpretation of this information would require detailed study by an industrial chemist.

Table 7. Process steps in the production of pesticides

	Fenoxaprop-P-ethyl	Acetamiprid	Azoxystrobion	Boscalid	Chlorfenapyr	Difenoconazole	Diflufenican	Dimoxystrobin	Fluroxypyr-meptyl	Imidacloprid	lufenuron	Nicosulfuron	novaluron	Tebuconazole	Topramezone
Acid chlorine formation															x
Acid cholorination				x				x							
Addition		x		x						x				x	
Amidation				x			x	x				x			
Amination		x							x						
Bromination					x	x									x
Carbamate formation												x			
Carboxylation															x
Condensation		x								x		x		x	
Coupling	x						x								
Chlorination		x	x	x	x		x	x		x		x	x		
Cyanation								x							
Cyclisation	x			x	x					x		x			x
Decarboxylation										x					
Dehydration			x												
Dehydrohalogenation	x		x			x	x	x				x			
Diazotisation				x			x			x					
Etherification	x				x		x						x		
Esterification									x						
Friedel Crfats reraction						x									
Fries rearrangement															x
Halogen exchange							x		x		x		x		
Hydrogenation														x	x
Hydroloysis							x	x	x						
Imine formation		x								x					
Isocyanate formation											x		x		
Isomer separation				x											
Methylation		x						x		x		x			
Nitartion				x			x			x	x				
Nitrile formation											x				
Oxidation													x		x
Oxime formation								x							x
Phosgenation	x									x	x	x	x		
Reduction				x	x		x				x				x
Ring Chlorination	x			x	x	x	x				x		x	x	
Sandmeyer reaction				x						x					
Sulfation												x			
Transesterification									x						
Urea formation											x				
Vilsmeier-Haackreaction										x					

METHOD 1

63.6 g of potassium tert.-butylate in 300 ml of dry methanol were introduced into a solution of 229 g of 2,4-dichlorobenzyltriphenylphosphonium chloride in 800 ml of dry methanol at 10° C., and 77.2 g of 4-chloroaceto-phenone were added after half an hour. The reaction solution was refluxed for 3 hours, the precipitated salt was filtered off at room temperature, the filtrate was evaporated down under reduced pressure, the residue was digested with petroleum ether at from 50° to 70° C. to free it from triphenylphosphine oxide, and the solution was evaporated down under reduced pressure.

The residue was taken up in 1 liter of carbon tetrachloride, and the solution was refluxed with 81.7 g of N-bromosuccinimide and 4 g of 2,2'-azoisobutyrodinitrile. After the reaction was complete, the succinimide was filtered off, the filtrate was evaporated down under reduced pressure and the residue was recystallized from methanol. 73.4 g (38.8%) of Z-1-(2,4-dichlorophenyl)-2-(4-chlorophenyl)-3-bromoprop-1-en e of melting point 128° C. were obtained.

METHOD 2

118 g of 2,4-dichlorobenzyl chloride were added dropwise to 14.6 g of magnesium turnings in 400 ml of dry diethyl ether at the boiling point. After the reaction was complete, a solution of 77.3 g of 4-chloroacetophenone in 400 ml of dry diethyl ether was added. Thereafter, decomposition was effected with aqueous ammonium chloride solution, the organic phase was separated off, washed neutral, dried over sodium sulfate and evaporated down under reduced pressure, the residue was taken up in 1 liter of toluene and the solution was refluxed with 4 g of 4-methylbenzenesulfonic acid, in a water separator. After dehydration was compelete, the toluene phase was washed with sodium carbonate solution and water and dried over sodium sulfate, the solvent was evaproated off and the residue was recrystallized from methanol to give 107 g (81.9%) of E-1-(2,4-dichlorophenyl)-2-(4-chlorophenyl)-prop-1-ene of melting point 84°-85° C.

METHOD 3

104 g of E-1-(2,4-dichlorophenyl)-2-(4-chlorophenyl)-prop-1-ene were refluxed with 62.3 g of N-bromosuccinimide and 5 g of 2,2'-azoisobutyrodinitrile in 1 liter of carbon tetrachloride, the precipitated succinimide was filtered off and the filtrate was evaporated down under reduced pressure. Treatment of the residue with methanol gives 91.5 g (69.4%) of Z-1-(2,4-dichlorophenyl)-2-(4-chlorophenyl)-3-bromoprop-1-en e of melting point 128° C.

METHOD 4

58.9 g of Z-1-(2,4-dichlorophenyl)-2(4-chlorophenyl)-3-bromoprop-1-ene were refluxed with 52.3 g of 3-choroperoxybenzoic acid in 590 ml of chloroform. After the reaction was complete, the chloroform phase was washed acid-free with aqueous sodium bicarbonate solution and water, dried over sodium sulfate and evaporated down under reduced pressure, and the residue was recrystallized from methanol to give two crystalline fractions:

4.1 41.3 g (70.2%) of 2-bromomethyl-2-(4-chlorophenyl)-3-(2,4-dichlorophenyl)-oxir ane (isomer A) of melting point 98°-99° C., and,

4.2 12 g (20.4%) of 2-bromomethyl-2-(4-chlorophenyl)-3-(2,4-dichlorophenyl)-oxir ane (isomer B) of melting point 93°-95° C.

Figure 1. Extract from United States Patent 4464381 for the active ingredient epoxyconazole.

Hypothesis: energy is requirement is related to molecular structure

Readily available data on molecular mass and structural metrics were obtained from PubChem (http://pubchem.ncbi.nlm.nih.gov/) to test for any relationship with energy requirements. For herbicides there was a weak correlation (r^2 = 0.25, or 0.42 if glyphosate is omitted) with molecular mass, but this was largely the result of a few points with high mass and high energy requirements and a “cloud” of points at lower masses (Figure 2). No relationship was found with any of the other variables individually. Linear and nonlinear models using combinations of variables did not improve the fit (measured by residual mean

squared error). No relationship between energy requirements and any of the variables was observed for insecticides and fungicides.

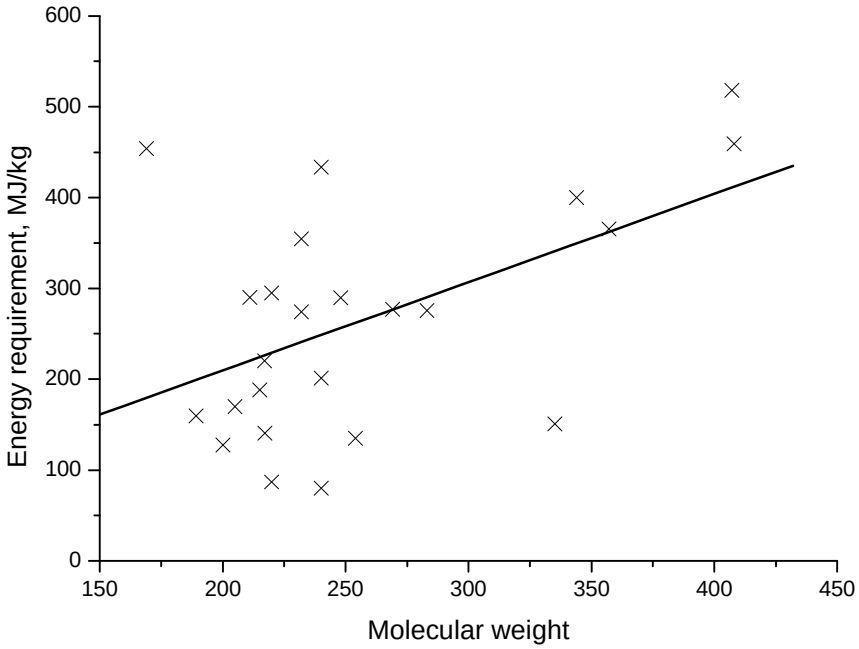

Figure 2. Total energy requirement for herbicide production (Green, 1987) versus molecular weight

It is possible that detailed analysis by an organic chemist would be able to identify measures of the difficulty of creating a specific chemical in terms for example of the position of a specific molecule on the carbon ring. However this level of detailed chemical analysis was beyond the scope of this project.

Hypothesis: energy requirement is related to year of discovery

Anecdotal evidence (van Laak, personal communication) suggests that the complexity and energy intensity of production has generally increased with time. This hypothesis was tested for the pesticides included in Green (1987) by plotting the total energy against the year when the chemical was first reported, as given by Tomlin (2003) and searches of the scientific literature using ISI Web of Knowledge and Google Scholar (Figure 3). A straight line was fitted to the data:

$$\mathbf{E = -399 + 10.8\ (Y\text{-}1900),} \qquad R^2 = 0.57$$

where E = energy in MJ/kg ai, Y is the year of reported discovery

No systematic differences were found between the three groups of chemicals (herbicides, fungicides and insecticides).

Using this formula with current pesticides and their recommended doses per hectare, Figure 4 shows that pesticide energy per hectare has reduced over time – indeed there are nowadays some very low doses, such that even 5000 MJ/kg ai would still result in reduced energy use per ha!

Note however that there is no data on these extremely active modern chemicals that are used at very low doses. It is therefore just as plausible that the energy required to produce these pesticides is much higher than predicted as that they are linear. However the hypothesis that pesticide energy per hectare per active ingredient is constant cannot be supported by Green's data.

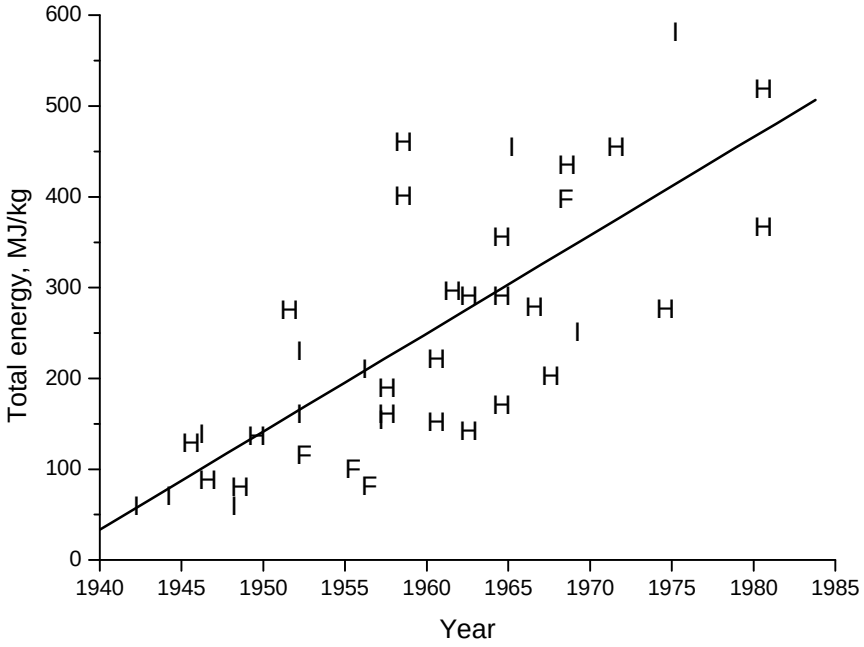

Figure 3. Total energy requirement for pesticide production (Green, 1987) versus date of first reporting. H: herbicide; F: fungicide; I: insecticide. Regression line: E = -399 + 10.8 (Y-1900), r^2 = 0.57.

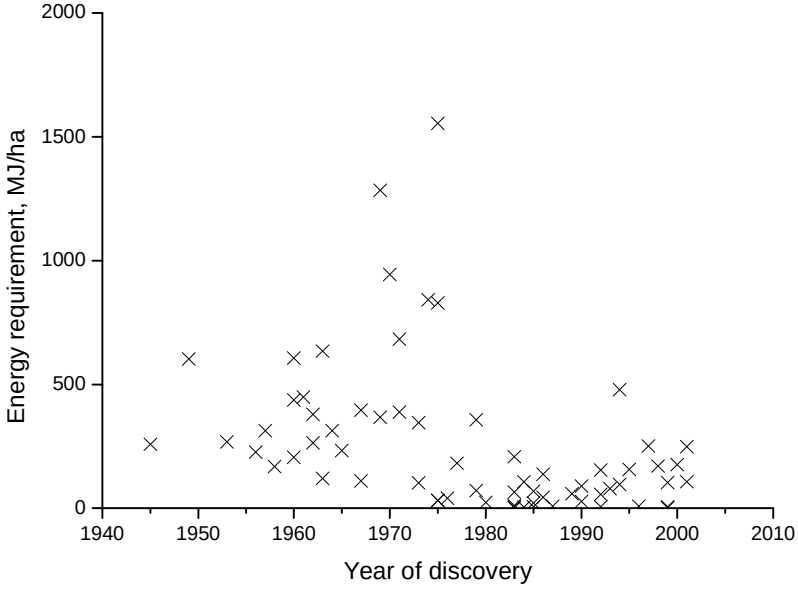

Figure 4. Energy requirements (MJ/ha) for pesticides against year of discovery, derived from regression of energy requirements for active ingredients on year of discovery and manufacturers maximum dose for arable crops

Conclusion and implementation

Of the methods tested, the only practical and effective one is to use the year of discovery, with the usual caveats related to linear extrapolation. Given the trend shown in Figure 3, it is likely that using energy requirements derived directly from Green, such as the mean or maximum will generally underestimate for chemicals introduced since 1985. However from this regression one would not expect any pesticide manufacturing energy to be over 1000 MJ/kg.

Using the same methods as above, dates were found for all the chemicals in the top 50 from the Pesticide Usage Survey (Garthwaite *et al*., 2006). The latest date was 2001, for which the energy requirement estimated by the regression was 713 MJ/kg. A value of 100 MJ/kg was used for dates before 1940, because use of the regression would predict negative values for dates before 1936.

Green's analysis (1987) considered that the energy for formulation, packaging and delivery would be around 20 MJ, and that given the errors in estimating production energy (he thought 10% for the best estimated chemicals), more detailed analysis was not warranted. We will therefore assume 20 MJ/kg ai for formulation, packaging and delivery.

Table 8 gives the resulting primary energy for production, formulation, packaging and delivery (MJ/kg ai) for the major pesticides reported by the Pesticide Usage Survey 2006 (top 50 by area or weight). Note that these are estimates derived from data that were themselves estimates 20 years ago and thus may contain significant errors. However even if an estimate can be shown to be high, that does not imply that they are all high, or vice-versa. While processes are likely to have become more energy efficient, chemicals have become more complex, requiring more energy. However, newer chemicals tend to be used at much lower application rates per hectare than earlier compounds.

Table 8. Primary energy used for production, formulation, packaging and delivery (MJ/kg ai) for the major pesticides reported by the Pesticide Usage Survey 2006 (top 50 by area or weight).

Function	Active substance	MJ/kg ai	Function	Active substance	MJ/kg ai
I&N	1,3-dichloropropene	226	H&D	Linuron	310
H	2-4D	107	GR	Maleic hydrazide	151
I&N	Alpha-cypermethrin	518	F	Mancozeb	280
H	Atrazine	208	H&D, H	MCPA	148
F	Azoxystrobin	615	H&D	Mecoprop-P	194
F	Boscalid	713	H&D	Mesosulfuron-methyl	659
H	Bromoxynil	302	H	Mesotrione	691
F	Carbendazim	410		Metalaxyl-M	659
H	Carbetamide	302	I&N, M&R	Metaldehyde	148
H&D	Chloridazon	291	H&D	Metamitron	432
GR	Chlormequat (+/-chloride)	270	H&D	Metazachlor	388
F	Chlorothalonil	313	F	Metconazole	615
H&D	Chlorotoluron	367	F	Metrafenone	713
I&N, I	Chlorpyrifos	324	H&D	Metsulfuron-methyl	518
H	Clopyralid	432	H	Nicosulfuron	594
H&D	Cyanazine	221	I&A&N	Oxamyl	345
F	Cymoxanil	442	H&D	Pendimethalin	421
I&N, I	Cypermethrin	600	H&D	Phenmedipham	345
F	Cyproconazole	551	F FST	Prochloraz	453
F	Cyprodinil	637	F	Propamocarb hydrochloride	464
H&D, H	Diflufenican	540	H&D	Propaquizafop	561
H&D	Diquat	420	H&D	Propyzamide	410
F	Epoxiconazole	626	H	Prosulfuron	626
	Ethephon	194	F FST, FST	Prothioconazole	475
H&D, H	Ethofumesate	367	F	Pyraclostrobin	702
I&N	Ethoprophos	334	H&D	Simazine	226
F	Fenpropimorph	475	F	Spiroxamine	669
H&D	Florasulam	691	S, F	Sulphur	
F	Fluazinam	594	SA	Sulphuric acid	
H&D	Flufenacet	648	I&N	Tau-fluvalinate	486
F FST	Fluoxastrobin	637	F FST, FST	Tebuconazole	551
H&D, H	Fluroxypyr	518	H&D, H	Thifensulfuron-methyl	540
F	Flusilazole	529		Tri-allate	270
H&D, H	Glyphosate	474	H&D	Tribenuron-methyl	540
GR	Imazaquin	518	H	Triclopyr	432
H&D	Iodosulfuron-methyl-sodium	691	H	Trifloxystrobin	680
H&D, H	Isoproturon	378	H&D, H	Trifluralin	171
F	Kresoxim-methyl	518	GR	Trinexapac-ethyl	583
I&N	Lambda-cyhalothrin	529	I&N	Zeta-cypermethrin	615

F= fungicide, FST = Fungicide seed treatment, GR = Growth regulator, H&D = herbicide and desiccant, I&N = Insecticide and nematicide.

4. Pesticide energy requirements of crops

The Pesticide Usage Survey determines the areas of crops to which a wide range of products are applied and thereby derives the weights of products applied to those crops. This typically accounts for about 90% of the chemicals applied, though for insecticides and nematicides, over half the mass of chemicals is in the category 'other'. Given the proportion of the active ingredient in each product, it is possible to calculate the weight of each active ingredient applied to each crop, and hence with the energy for the active ingredient (Table 2, Table 8), the energy per area of each crop.

Table 9 illustrates this calculation for azoxystrobin, for the four products containing this active ingredient. The survey gives the weight of active substance for each of the four products, but in the formulated mixtures this is the total of both active ingredients. The proportion of azoxystrobin in the product is used to determine the weight applied. For example, in the case of wheat, 123.59 t of azoxystrobin + chlorothalonil contains 123.59 x 100 / 600 = 20.66 t of azoxystrobin. Summing the values for the four products gives a total of 54.4 t of azoxystrobin applied to all wheat in the UK, with an energy input, using the value from Table 8, of 33.5 TJ.

Summing these values over all active ingredients, gives the total pesticide energy input to each type of crop by category of pesticides, Table 10. This is 1681 MJ/ha for wheat.

Given the assumptions that have had to be made there is some uncertainty in these numbers. The lower section of Table 10 shows the same calculation using the average 241 MJ/kg ai from Green's data with the actual weights of pesticides applied from the survey, which is considerably lower – for wheat this is 1130 MJ/ha. The standard deviation of the average from Green is 140 MJ/kg. Audsley (1997) used the method of averages of categories of pesticides with the actual rates of pesticides expected to be applied to an intensively managed crop of wheat. This resulted in 1503 MJ/ha of pesticide energy required for wheat. From the analysis of energy used per active ingredient, the maximum level was approximately 700 MJ/kg, which if it was applied to all pesticides at current dose rates gives 3281 MJ/ha for wheat. It therefore seems reasonable that 1130 is a minimum and 3281 is a maximum value for wheat. Other crops would be pro rata.

Williams *et al* (2006) calculated that for the average mix of types of energy into pesticide production according to Green (1987), the Global Warming Potential (100 years) was 0.069 kg CO_2e per MJ pesticide energy. Since there is no other information of how the mix of energy types and precursors is used in current pesticide manufacture, this figure will be used.

Table 9. Calculation of the pesticides and hence pesticide energy input of Azoxystrobin to arable crops in the UK (Garthwaite *et al.*, 2006)

	Azoxystrobin	Azoxystrobin /chlorothalonil	Azoxystrobin /cyproconazole	Azoxystrobin /fenpropimorph
Crop area, ha				
Wheat	276397	220655	80844	24187
Winter barley	37484	9494	15051	17671
Spring barley	22358	11045	9045	10492
Oilseed rape	62889	0	3923	0
All potatoes	19673	0	0	0
Peas	27173	1819	0	0
Beans	52512	835	0	0
All crops	**528605**	**247691**	**125183**	**52995**
Concentration in product, g/l		100	200	100
		500	80	280
Weight of active substance, t				
Wheat	24.54	123.59	10.16	7.48
Winter barley	3.6	4.48	1.42	5.74
Spring barley	1.92	5.39	1.24	2.88
Oilseed rape	9.61	0	0.8	0
All potatoes	12.78	0	0	0
Peas	3.08	1.31	0	0
Beans	7.3	0.54	0	0
All crops	**66.7**	**137.35**	**16.68**	**16.26**
Weight of active ingredient per crop, t				
Wheat	54.4			
Winter barley	6.9			
Spring barley	4.5			
Oilseed rape	10.2			
All potatoes	12.8			
Peas	3.3			
Beans	7.4			
All crops	**105.8**			
Energy input as azoxystrobin per crop, TJ				
Wheat	33.5			
Winter barley	4.2			
Spring barley	2.7			
Oilseed rape	6.3			
All potatoes	7.9			
Peas	2.0			
Beans	4.5			
All crops	**65.1**			

Table 10. Pesticide energy input to arable crops per hectare, derived from Pesticide Usage Survey 2006

	Fungicide	Herbicide	Insecticide	Molluscide	Growth regulator	Seed treatment	TOTAL
Wheat	475	792	28	11	340	35	**1681**
Winter barley	301	802	10	2	230	15	**1359**
Spring barley	254	225	6	0	18	14	**516**
Oats	130	154	6	0	201	21	**512**
Rye	85	1005	11	2	97	20	**1220**
Triticale	63	248	3	0	36	7	**357**
Oilseed rape	188	752	17	29	0	15	**1001**
Linseed	42	756	4	0	0	132	**934**
Potatoes	2912	896	751	37	132	154	**4883**
Peas	330	979	31	0	0	60	**1401**
Beans	363	645	15	1	0	0	**1025**
Sugar beet	66	2283	18	1	0	300	**2667**
Set-aside	32	395	3	5	1	4	**439**
Forage Maize	0	540	4	1	0	27	**571**
Calculated energy per hectare using average 241 MJ/kg ai from Green's data							
Wheat	269	511	19	17	297	16	1130
Winter barley	151	498	5	2	197	7	861
Oilseed rape	87	447	7	47	0	7	596
Potatoes	1838	548	794	51	79	67	3376
Calculated energy per hectare using 700 MJ/kg ai							
Wheat	782	1485	54	51	864	46	3281
Winter barley	440	1447	14	7	573	19	2500
Oilseed rape	254	1290	22	136	0	19	1721
Potatoes	5338	1592	2306	147	229	195	9806
Calculated energy per hectare by Williams & Audsley, 2007							
Wheat							1335
Winter Barley							1068
Oilseed Rape							610
Potatoes							3363
Weighted average pesticide production energy, MJ/kg ai							
	423	**386**	**274**	**154**	**276**	**511**	**370**

5. Life cycle inventory of arable crops

The values from Table 10 were inserted into the Cranfield Life Cycle Inventory (LCI) model of major arable crops (Table 11). (www.agrilca.org) A life cycle assessment calculates the resource use and emissions to the environment from the production of crops *per tonne of crop*, and traces resource use back to the resources needed and emissions from extraction, production and delivery of inputs to the actual agricultural system. Since any change in the state of the soil must also be accounted for, the method implicitly requires that the agricultural system is in steady state over a crop rotation – thus soil organic matter and weed seed content must not increase or decrease. This is achieved in practice using crop-soil simulation modelling.

The results show that pesticide manufacturing represents about 9% of the energy use of arable crops – less for spring crops and more for potatoes. The amount represents about 100-200 MJ/t of crop. Given the above maxima and minima, the range is no lower than 6% and no higher than 16%.

Pesticide manufacturing represents about 3% of the 100-year Global Warming Potential (GWP) from crops. This is because about 50% of the GWP from arable crops is due to the field emissions of nitrous oxide from the soil which has a very large GWP. Nitrous oxide emissions are a consequence of parts of the nitrogen cycle in the soil in which nitrate is reduced or nitrate precursors are partly oxidised. The whole cycle includes organic matter which is converted by microbes in the soil into nitrate which can be utilised by crops.

Paveley *et al (*2008) estimated that fungicide use saved the need for 500-1000 kg CO_2e per hectare which would otherwise be needed to maintain current levels of production of wheat. This compares well with the 33 kg CO_2e/ha resulting from manufacturing the fungicides. Similarly Wilson & Sparkes (2007) showed that organic farming emits 220 kg CO_2e/ha in the process of weed control whereas the manufacture of chemical herbicides amounts to 55 kg CO_2e/ha.

Table 11. Life cycle inventory of major crops (per tonne at the farm gate) with new pesticide data showing proportion of burdens due to pesticides

	Bread Wheat	Feed Wheat	Winter Barley	Spring Barley	Oilseed Rape	Potatoes maincrop	Potatoes 1st Earlies	Potatoes 2nd Earlies	All potatoes	Field Beans	Maize Silage
Summarised values per t											
Energy used, MJ	2567	2351	2467	22478	5468	1531	1,493	878	1465	2602	1732
GWP, kg 100 year CO_2e	551	491	449	399	1131	150	216	115	165	491	325
EP, kg PO_4 Equiv.	2.9	2.8	2.3	2.0	8.6	0.4	2.0	0.5	0.9	5.8	1.8
AP, kg SO_2 Equiv.	2.6	2.2	2.2	1.4	7.4	0.5	0.6	0.3	0.5	2.2	1.2
Pesticides used, dose ha	0.8	0.8	0.8	0.3	1.0	0.4	0.6	0.4	0.5	1.2	0.3
Abiotic depletion, kg Sb Equiv.	1.3	1.2	1.3	1.2	2.5	0.9	0.6	0.4	0.8	1.4	1.7
Land, ha	0.14	0.13	0.16	0.18	0.32	0.02	0.04	0.04	0.03	0.31	0.09
Proportion of emission from pesticides, %											
GWP, kg 100 year CO_2e	**2.9**	**3.0**	**3.5**	**1.8**	**1.9**	**6.5**	**6.7**	**9.3**		**4.4**	**1.1**
Summary of energy consumption by activity, %											
Field diesel	24	25	27	32	26	22	45	43	30	52	29
Machinery manufacture	10	11	12	14	10	7	13	13	9	22	10
Crop storage & processing	5	5	6	7	3	45	0	0	29	6	4
Pesticide manufacture	**8.9**	**9.2**	**8.7**	**4.1**	**6.5**	**8.2**	**12.5**	**12.5**	**9.8**	**12.5**	**3.1**
Fertiliser manufacture	52	50	47	43	55	18	28	27	21	7	54
Field diesel (or drying fuel), MJ/t											
Cultivation	396	358	415	455	879	110	230	118		882	270
Spraying	53	48	42	33	114	22	37	24		81	46
Fertiliser application	54	49	60	69	121	91	137	84		124	36
Harvest	136	124	147	164	284	71	175	98		276	142
Grain storage	115	109	128	128	131	525	0	0		141	76
Manufacturing, MJ/t											
Cultivation	134	121	142	158	292	27	57	29		295	89
Spraying	41	37	32	25	89	14	22	15		63	36
Fertiliser application	17	15	19	20	43	10	14	9		33	10
Harvest	89	81	95	107	137	40	73	42		184	37
Grain storage	21	20	20	20	20	70	0	0		21	0
Pesticide manufacture	**240**	**217**	**214**	**93**	**353**	**108**	**159**	**116**		**325**	**53**
Fertiliser manufacture	1390	1172	1153	976	3004	235	365	205		179	938

GWP= Global Warming Potential, EP= Eutrophication Potential, AP = Acidification Potential

6. Conclusion: Standard values for pesticides for use with Life Cycle Inventories of arable crops

This report provides new values for pesticide production energy use. Table 8 provides values for specific active ingredients that can be used where the amount of pesticides used per crop changes. Further values for new actives can be estimated from the linear regression, with the proviso that very recent discoveries are likely to be somewhat unreliable.

Table 12 provides pesticide energy inputs to crops by type of pesticide. Note that this represents current surveyed practice by farmers. It thus includes a range of practices – overestimating energy use by some and underestimating energy use by others. Thus farmers with weed problems would be likely to apply more herbicides than the average. Farmers in disease prone areas would be likely to apply more fungicides than the average.

Table 12. Standard pesticide energy input to arable crops, MJ per hectare

	Fungicide	**Herbicide**	**Insecticide**	**Molluscide**	**Growth regulator**	**Seed treatment**	**TOTAL**
Wheat	475	792	28	11	340	35	**1681**
Winter barley	301	802	10	2	230	15	**1359**
Spring barley	254	225	6	0	18	14	**516**
Oats	130	154	6	0	201	21	**512**
Rye	85	1005	11	2	97	20	**1220**
Triticale	63	248	3	0	36	7	**357**
Oilseed rape	188	752	17	29	0	15	**1001**
Linseed	42	756	4	0	0	132	**934**
Potatoes	2912	896	751	37	132	154	**4883**
Peas	330	979	31	0	0	60	**1401**
Beans	363	645	15	1	0	0	**1025**
Sugar beet	66	2283	18	1	0	300	**2667**
Set-aside	32	395	3	5	1	4	**439**
Forage Maize	0	540	4	1	0	27	**571**
Weighted average	**396**	**706**	**41**	**10**	**175**	**36**	**1364**
Weighted average pesticide production energy, MJ/kg ai							
	423	**386**	**274**	**154**	**276**	**511**	**370**

It must be noted however that the range of uncertainty on these values is huge. It is not implausible that pesticides represent 6% to as much as 16% of the energy input to arable crops. There would thus be considerable benefit to more detailed information on the energy required for the manufacture of some current pesticides. This may be possible by repeating the method of analysis of Green using patent data on modern pesticides, in conjunction with an industrial organic chemist, but actual plant data would be preferable. Indeed the latter is essential for use is a procedure for "carbon footprinting", such as that being sponsored by the Carbon Trust and Defra in the BSI's Publicly Available Specification PAS2050.

A factor of 0.069 kg CO_2e per MJ pesticide energy can be used to convert these to the Global Warming Potential (100 years), which is thus a weighted average of 94 kg CO_2e per hectare of arable crop.

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