SOME PROBLEMS IN THE COMPILATION OF A COMPATIBILITY CHART OF ORCHARD SPRAY CHEMICALS FOR USE IN BRITISH COLUMBIA¹

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This paper arises out of discussions that took place when the compatibility chart of spray chemicals for orchardists in the British Columbia interior was drawn up in 1957; I was secretary of the committee responsible for producing the chart. This chart has to be revised at intervals, though not necessarily annually, as new materials and new formulations are introduced, and so it is worthwhile trying to put on paper some of our thoughts as to the principles involved.

In this paper, therefore, the examples quoted relate almost solely to experience in British Columbia while the opinions expressed represent an attempt by the author to summarize his own conception of the substance of numerous discussions between members of the Summerland Entomology Laboratory and of other agricultural scientists concerned with fruit growing in British Columbia. A review and discussion based on a broader geographical basis, perhaps world-wide, and on a broader range of crops, would be most desirable. This, however, would represent a much more ambitious project than is intended here.

One of the first things to appreciate about "compatibility" in connection with spraying of pesticides, is that the word covers a number of criteria and that materials that are compatible according to one criterion, are not compatible according to another. Compatibility of spray material is not a relatively simple concept as is "compatibility" of rootstock and scion in horticulture.

Chemical Compatibility

Primarily, compatibility is thought of as chemical compatibility, e.g., if two chemicals react in such a way as

to reduce the effectiveness of one or both, then the two chemicals are incompatible. Thus, if certain fungicidal copper compounds are mixed with lime-sulphur (a mixture of calcium polysulphides) copper sulphide is formed which is insoluble, and useless (37). However, in general, the changes that take place on mixing spray materials may be very complex and even purely chemical compatibility can turn out to be a complex matter. In practice, a spray chemical does not consist of one compound, but is a "formulation." The need for formulation arises from the fact that most of the newer miticides, insecticides and fungicides are insoluble in water (20) and water is the vehicle most commonly used in applying them. They may be, therefore, sold dissolved in organic solvents such as xylene to which a small amount of emulsifier, such as an alkyl aryl polyether alcohol, is added (36). When mixed with water in the tank of the sprayer, such a formulation forms an emulsion. Alternatively, the active ingredient may be mixed with a suitable finely-divided, inert carrier acting as an absorptive material because of the large surface area of the fine particles (for example, aluminum magnesium silicate) together with a small amount of wetting agent such as an alkyl phenyl ether of polyethylene glycol (6). The formulation is sold as a co-called "wettable powder" which, on mixing with water in the spray tank, becomes a suspension of limited stability that is prevented from settling mainly by mechanical agitation. Since the type of formulation influences the effectiveness of the pesticide (10) it is obvious that on mixing two formulations, the possibilities for chemical and physical reactions that will affect the performance of one or both of the pesticides complex. Generally speaking, are chemical compatibility is, in practice,

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the compatibility of materials that are already mixtures. It is not so simple as saying that sodium chloride and silver nitrate are incompatible because the insoluble silver chloride is percipitated.

There is another problem—a practical one-of chemical incompatibility. Chemists may say definitely that two materials are incompatible because they decompose during or after mixing. However, in practice the rate of decomposition is exceedingly important. Thus, according to McArthur and William (25), parathion [0,0-Diethyl O-p-nitrophenyl phosphorothioate] breaks down extremely slowly when mixed with lime-sulphur in the laboratory. If a tankful of the mixture is sprayed without unreasonable delay. both materials are effective. On the other hand, mala-[S-(1,2-Dicarbethoxyethyl) thion O,O-d i m e t h y l phosphorodithioate breaks down so rapidly in lime-sulphur that only 25 per cent of the malathion remains as such approximately one hour after mixing (25). From the grower's point of view, as well as the chemist's, these two materials are incompatible. All so-called organic phosphates will, in time, break down in alkaline solutions like lime-sulphur, but it is the rapidity of breakdown that is important.

Malathion deserves further mention. It hydrollyses very easily, not only in alkaline solution but even in acid, and, to some extent, in water (20). In the presence of iron the hydrolysis is catalysed to such a degree that malathion emulsion must be sold in glass, and not in iron containers (20). The ease of hydrolysis makes production of wettable powders of malathion particularly difficult. This is why malathion is an expensive material to formulate as a wettable powder and costs more than parathion. The emulsion form in glass bottles is generally cheaper.

Mention should also be made of nicotine as used in British Columbia. Nicotine sulphate is acid, and, on most charts therefore, indicated as

compatible with organic phosphates. However, it was found that, under conditions of the British Columbia interior, nicotine sulphate could be made a more effective aphicide by the addition of sodium carbonate. which reacts with nicotine sulphate to release free nicotine. At temperatures above 70°F., and particularly when applied as a concentrate spray by an air-blast machine, nicotine is extremely toxic to aphids (23). However, nicotine sulphate-sodium carbonate mixture is alkaline and should not be used with organic phosphates or with other pesticides that break down in alkaline solution (25).

Some of the so-called minor elements—zinc, manganese, magnesium, boron—can be applied as dissolved salts with an orchard sprayer to nutrition-deficient trees. Soluble dinitro compounds such as sodium dinitro-O-cresylate, if added to such salts, tend to react to produce insoluble metallic compounds that are unavailable to the plant and are but slightly toxic to insects. However, the two types of materials are not applied at the same time (2).

This brings up a point for discussion. Why express an opinion on the compatibility of two materials that should never be applied at the same time? Some comprehensive charts show compatibilities, or otherwise, of highly unlikely mixtures. We feel it is better to discourage the grower from wasting money and risking damage from the use of such mixtures by indicating that the two materials are not normally applied together.

Phytotoxic Incompatibility

When some pesticides are mixed, no chemical change may take place that reduces the effectiveness of the ingredients, but the mixture may cause damage to the plant. This is often a physical phenomenon in that the solvent, or adjuvant, in one formulation may allow increased pentration of some component in the other formulation. Many oils, for instance, readily penetrate the underside of a leaf particularly through the stomata (11) and so transport anything dissolved in them. Lighter oils will readily penetrate either leaf surface and twigs as well (40). It is not surprising, therefore, that many oils do damage to fruit trees (5) and the selection of suitable types of oils, for both dormant and summer spraying, occupied the attention of orchard entomologists for many years. Thus, summer oil can cause plant damage, and so can wettable sulphur, but a combination of the two is far worse than one would expect from a purely additive response. This effect of this particular combination is so marked (12) that some of our older spray calendars, published at a time when application of summer oil was more common, included a warning not to apply sulphur (or lime-sulphur) and summer oil, even separately, within a certain time in order to avoid spray injury (1). In place of the summer oil, any organic solvent from another formulation can act with sulphur in the same way. The high toxicity of DNOC [2-methyl-4, 6-dinitrophenol] is well known (5, 20) and, though it could be used by itself with care as a summer spray in orchards (26), it has not been so recommended because the presence of a very small amount of oil, as in spray-drift from a neighbors orchard (9), or the presence of slight oil residue from a much earlier spray appliproduce (29),will severe cation symptoms of phytoxicity. And oil or oil-like components in formulations of other pesticides act similarly on DNOC. Incidentally, such deep penecontact insecticides is, tration of generally speaking, of little value insecticidally as most insects or mites. or their eggs, are on the surface of the plant.

We have, for instance, listed malathion as incompatible with dinitro compounds because malathion is marketed most cheaply as an emulsion, and the solvent in the emulsion allows the dangerous penetration of the dinitro compound. Malathion emulsion in combination with glyodin [2-Heptadecyl-2-imidazoline acetate] and captan [N-Trichloro-methylmercapto-4-cyclohexene-1, 2-dicarboximide] appears to be more phytotoxic than a purely additive response would imply. Sevin [N-methyl-1-naphthyl carbamate] and lime-sulphur are incompatible because, in alkaline solution, the former breaks down fairly rapidly to alpha-napthol (39) which is decidedly toxic to some apple varieties, although Sevin itself is not. There is also some slow breakdown of Sevin alone to alpha-napthol because of weathering and this has caused slight injury on some varieties of apple, e.g., McIntosh (39).

A somewhat similar case, though not of phytotoxicity, is the evidence (33) that tainting from lindane [1,2,3, 4,5,6-hexachloro-*cyclo*hexane] is accentuated in the presence of summer oil, added to increase the aphicidal properties (27), presumably a result of increased penetration.

On the other hand, damage with minor elements probably is rarely accentuated by incompatibilities for the damage is believed to be due to exosmosis and would take place with any strong salt on the leaf.

In some combinations that are prone to cause damage, for instance ovex [p-Chlorophenyl p-chorobenzenesulphonate] with malathion, or with ferbam [ferric dimethyldithiocarbamate], there is no evidence, considering the extent of the damage, that more than a purely additive response is involved (9). However, even in such a case, some warning to the grower is required. It seems unlikely that in a mixture of ingredients, all phytotoxic to some degree, overall phytotoxicity will be reduced.

Physical Incompatibility

An example of physical incompatibility arises in the mixing of limesulphur and dormant oil. If oil that is emulsified by a soap or soap-like compound is added to a solution of limesulphur, the calcium in the limesulphur reacts with the emulsifier to produce a calcium soap and may cause the emulsified oil to invert. In that case there will be an emulsion of water drops in oil instead of oil drops in water; and, because the continuous phase is oil, the emulsion will float on top of the bulk of the water as a scum (19).

At this point, before considering other aspects of compatibility, it is worth noting that manufacturers seem to be conservative when describing the compatibilities of a new material. Though they may well tend to exaggerate its pesticidal potencies, they have nothing to gain by risking its being mixed in some deleterious combination that may merely bring their product a bad name. This means that the grower may have to make separate applications in order to avoid stated incompatibility and so he incurs unnecessary expense. However, from the manufacturer's point of view, a product is not usually sold on the strength of its wide compatibility; it is sold on reputed efficiency in killing disease organisms or insect pests. For instance, DDT is often stated to be incompatible with lime-sulphur, but the actual decomposition is so slow as not to be a factor.

Other Spraying Problems

The categories of incompatibility that have been lisited above are conventional ones, and the necessary information can generally be included in some way, in the conventional type of two-dimensional chart. There are, however, closely related problems of spraying which usually need to be dealt with at the same time, but which do not solely concern combinations of two or more spray materials. We can, if we like, stretch the word "incompatibility" to include these problems; but, whether we do or not, these problems should be discussed at the same time.

(a) Some questions arise from the use of a particular type of sprayer. We might refer to these as problems of "m e c h a n i c a l incompatibility." Thus, in the air-blast concentrate sprayer, difficulties of excess foaming sometimes arise, difficulties that do not arise in the old-type, high-volume, gun sprayers. For instance, Sulphenone [p-chlorophenyl phenyl sulphone] has to be applied at high rates for

mite control (2, 7). As DDT [2,2-Bis(pchlorophenyl-1, 1, 1-trichloroethane and perhaps ferbam, are likely to be applied at the same time (2), the total quantities of emulsifiers and wetting agents in the tank are very large; excessive foaming is the result (25). The material, ryania (ground stems of Ryania speciosa Vahl.), has caused trouble simply by the concentration of solid suspension in the tank. For instance an application of ryania at 48 pounds per acre for codling moth control in British Columbia (28) meant that there were 48 pounds of insoluble and bulky powder in 80 gallons of water. DNOCHP [2,4-dinitro-6-cyclohexyl phenol] formerly recommended for the control of several species of mites (1) is one of the few spray chemicals unsuited for concentrate application because of enhanced phytotoxicity (7). On the other hand, under some circumstances phytotoxicity is reduced by true concentrate application (i.e., no leaf drip as compared with dilute high-volume application for the same per acre amount of material (21, 23).

(b) "Seasonal Incompatibility". Many materials are safe at one stage of plant development, but liable to cause damage at another; dormant oils are an obvious example. Ovex is ovicidal at the pink bud stage, and in the summer, but because of the likelihood of fruit damage (8), can only be recommended in the former case. Other miticides such as Aramite [2-(*p*-tert.-Butylphenoxy)-isopropyl 2'chloroethyl sulphite] are non-ovicidal and would be of little value in the early part of the season (7).

(c) "Weather Incompatibility". Dinitro compounds and lime-sulphur must dry quickly if injury is to be prevented. That, in fact, is the reason that lime-sulphur is applied in England by concentrate sprayer, completely undiluted (23). The general recommendation in British Columbia is not to apply lime-sulphur spray concentrate when leaves are wet (2).

In warmer climates, wettable sulphur can cause injury to many crops (19) and in British Columbia is likeENTOMOLOGICAL SOCIETY OF BRITISH COLUMBIA, PROC. (1959), Vol. 56, Nov. 4, 1959

ly to do so to fruit-tree foliage during hot summers. For many years the spray calendar (1, 2) has contained a warning to this effect.

At high summer temperatures nicotine is a very effective aphicide but in cool weather it gives poor aphid control in orchards (21, 24, 34).

(d) "Crop and Variety Incompatibility". Some crops or varieties are particularly likely to suffer damage from a particular spray chemical regardless of whether it is combined with other materials. For instance, malathion is likely to damage cherry, either as a wettable powder or as an emulsion (34). Diazinon [O, O-Diethyl O-(2-isopropyl-4-methyl-6-pyrimidyl) phosphorothioate] is generally safe on cherry as a wettable powder, or an emulsion (31), but under the moister conditions of the Kootenay district, the latter has caused damage (38). Aramite is safe on apples but can cause damage on pears (2, 7). Pears, especially of the Anjou variety, are also more susceptible to injury from dinitrophenol derivatives than apples (26). Lead arsenate, once widely used on apples, is phytotoxic to peach and apricot (35). Maneb may be injurious to some varieties of apples, particularly Rome Beauty. Golden Delicious apple is susceptible to injury by many materials, for instance, by trithion [O, O-Diethyl S-p-chlorophenylthiomethyl phosphorodithioate] either as an emulsion or wettable powder (32). Fruit damage is a particularly important consideration because sales organizations demand a very high standard of finish and a freedom from blemish—a problem not met with in many other crops.

(e) "Geographical Incompatibility". This is perhaps a vague category because not only climate varies with geographical locality, but so do soil, orchard practices, varieties, times of application, species of pests and types of applicator. However, it is clear that some general differences are important. Thus, lime-sulphur and oil are applied regularly to peaches in California, but used in British Columbia the same mixture would cause damage (35) and is not recommended (2).

Rapidity of drying in different localities may influence the choice of spray chemicals. Characteristic varieties in different localities may cause different materials to be regarded as safe or dangerous. In England, certain apple varieties including Worcester Pearmain and James Grieve (30), are seriously damaged by the mite ovicide, fenson [p-Chlorophenyl benzene sulphonate] in the pink bud stage (18). However, fenson is not injurious at the pink bud stage to common varieties of apple in British Columbia and is here regarded as less likely to cause damage than the somewhat chemically similar ovicide, ovex (8).

The preceding examples in this section are examples of difficulties arising from spraying that are not, strictly speaking, the result of incompatibility; but they emphasize that the grower must concern himself with all troubles associated with spraying, and incompatibility, as ordinarily defined, is one of these. The grower wants to know if he will get effective control and no damage from chemicals A or B; or from a mixture of A and B, irrespective of whether conventional conceptions of compatibility are involved. Therefore, along with a suitable local compatibility chart, there should be a brief summary of general and specific advice about dangers that are not apparent from inspection of the chart alone. This summary should be regarded as equally important to the chart. Without it a grower may be inclined to regard the chart as a complete guide to the dangers associated with spray mixtures; this it certainly is not.

Presentation for the Grower

When we have acquired all the data we think relevant, we are next faced with the problem of presenting the information to the grower. We do not think that a broad, comprehensive compatibility chart covering all crops, areas, and chemicals is of any great value. Such a chart must have so many reservations and warning categories as to be of doubtful value except in the most obvious cases. Moreover, a large compatibility chart cov-

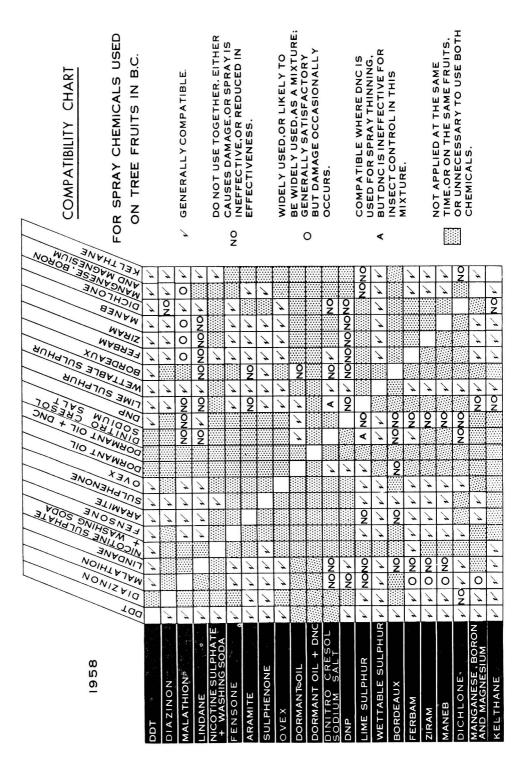


Fig. 1.-Compatibility chart of orchard spray chemicals for use in British Columbia.

ering many more chemicals than are used in British Columbia will merely confuse the grower; consequently, the chart, or charts, should be as simple as possible. In some fruit growing areas where many chemicals are in use, some simplification has been reached by issuing charts for each tree-fruit. This has been done, for instance, in New Zealand by Jacks and associates (14, 15, 16). Borden (4) in California produced a compact chart of reasonable size covering all tree-fruits and nuts, but consisting of two sections-one covering dormant and prebloom sprays, and the other post-blossom applications. Both the New Zealand and California charts covered a larger number of chemicals than are used in British Columbia. In addition to the charts for specific fruits, Jacks (13) also issued a booklet giving general warnings on incompatibilities for all crops.

Examination of the present British Columbia spray recommendations for orchardists (2), shows that 11 materials are listed for use as sprays on cherries, ten on prunes, eight on apricots, 16 on peach, and 19 on apples and pears. These, of course, include alternatives; only a few would be used by any one grower. All materials that can be applied to stone fruits can be, with only one or two exceptions, applied to apples. And in addition, almost all fruit growers in the British Columbia interior grow apples, though not all grow stone fruits. About five materials, not on the 1958 spray chart, are also in fairly common use. In view of the modest number of materials recommended in British Columbia, it was felt that one chart could cover all tree-fruits. Separate smaller charts for each stone fruit would not be justified because very few growers earn a living from one kind of stone fruit only.

A decided stand was taken to express no opinion on the compatibility of materials not used together, but to insert a symbol on the chart indicating "not applied at the same time, or on the same fruits, or unnecessary to use both materials". This approach should help the grower to avoid error

and expense in the use of a wrong, or unnecessary material, and discourage him from using unusual mixtures that might damage his fruit.

The category "spray with caution" so prevalent on many comprehensive charts, we consider to be almost useless. If a grower could detect, within a few minutes of commencing to spray with some questionable combination. any plant injury or lack of pest control, and could thereupon discontinue his efforts, there might be some point in the warning. However, in practice, the effectiveness, or damage that results, is not, as a rule, apparent until several days later. When there is reasonable likelihood of damage, we feel that the materials should be listed as incompatible. Now that rapid application by concentrate sprayer (23) is common it is then well worth the grower's time to put on separate spray applications rather than risk damage. On the rare occasions when a grower might be likely to use a doubtful mixture and take a calculated risk, the possibility of damage would be indicated.

A compatibility chart based on considerations of this kind was issued in 1957 (3). Since then, a few extra materials have been added to the list and the extent of the use of others enlarged. A modified chart incorporating these recent changes is shown in Fig. 1. In this chart all currently recommended spray materials are listed. In addition, older materials, though not recommended but widely used, are also included. Obsolete materials still used by a few growers are not listed, nor is the highly toxic compound, parathion, though it is quite commonly applied. As it is the firm, if unique, policy in British Columbia not to recommend highly toxic materials (21) particularly because of dangers to human beings in the typically small orchards and in home sites, it was considered that nothing further should be done to apparently sanction the use of such materials.

General Advice on Spraying and Compatibility

Under the heading "Information on

Compatibility, Spray Damage and Related Problems", information, of the type mentioned earlier that covers points not apparent from the chart, was noted on the back of the chart issued in 1957. Since then a number of omissions have been noted. The following items of information, and recommendations for growers, are suggested for the next chart to be issued:—

- 1. Lack of "compatibility" may be apparent in several ways. Combinations are incompatible (a) if they cause damage when the separate ingredients do not (b) if the combination causes a reduction of effectiveness of either ingredient (c) if there are other troubles such as excess foaming in the tank, or breaking of an emulsion, that make spraying difficult.
- 2. Almost all spray materials may, under unfavourable conditions, cause injury.
- 3. Unrecommended combinations may sometimes be harmless or satisfactory. They may also be disastrous.
- 4. Some spray materials are prone to cause injury; in a combination this may be confused with incompatibility.
- 5. Under British Columbia conditions, emulsions or solutions are generally more likely to cause damage than wettable powders. In combinations this tendency may be increased.
- 6. Liquid surface-active adjuvants or "surfactants" (in excess of the normal adjuvant in an emulsion or wettable powder), added by growers to spray concentrates to improve finish and effectiveness. are likely to accentuate injury from materials that are themselves prone to cause injury; or if spraying is continued, to dripping; concentrates containing ferbam, malathion, DNOCHP, or lime-sulphur are particularly suspect in this connection.
- 7. Once a tank of spray material is mixed, apply as soon as possible.

- 8. Do not spray potentially harmful materials when foliage is wet.
- 9. Spray in still air if possible.
- 10. Excess foaming may occur in the tank if several materials are mixed, as each may contain a highly-foaming wetting agent. Certain types of wettable sulphur are liable to foam excessively in concentrate sprayers.
- 11. Dormant oil may cause injury to fruit buds if applied too late, and particularly if improperly emulsified or double-sprayed. Application in windy conditions may result in double spraying.
- 12. Malathion should not be used on cherries. On other fruits, a wettable powder is less likely to cause injury alone, or in mixtures, than are liquid formulations. Malathion decomposes very rapidly in alkaline solutions such as lime sulphur, and becomes ineffective.
- 13. Nicotine sulphate should always be used with washing soda for maximum effectiveness in concentrate spraying. This is a basic, not acid, mixture and incompatible with many other materials. Most compatibility charts refer to the use of nicotine sulphate alone; it is acid, and behaves differently.
- 14. Nicotine should not be applied at temperatures below 70°F. or ineffective control may result.
- 15. Lindane is not now recommended because of its tendency to taint fruit, especially processed fruit.
- 16. Aramite should not be used on pears*.
- 17. DNOCHP should not be applied (a) with concentrate sprayers (b) to pears until four weeks after the calyx stage (c) to apples until two weeks after the calyx stage (d) with summer oil or after oil (e) with added surface-active adjuvants. DNOCHP may react with basic or metallic compounds.

30

^{*}This was the recommendation up to 1958. Because of a possible carcinogenic hazard, the Canadian Food and Drug Directorate prescribed, early in 1959, a legal residue tolerance of zero for Aramite. Aramite is not now recommended at all in British Columbia.

ENTOMOLOGICAL SOCIETY OF BRITISH COLUMBIA, PROC. (1959), VOL. 56, NOV. 4, 1959

- 18. Lime-sulphur should not be applied as a concentrate when trees are wet, or in damp weather.
- 19. Ovex and fenson should not be applied after the pink bud stage to any fruit.
- 20. Maneb can cause injury to apples of the Rome, Cox's Orange and Wagener varieties.
- 21. Ferbam leaves a more objectionable residue than ziram. Husk fall application of ferbam to stone fruits must not be delayed or unmarketable fruit may result from discoloration.
- 22. The information presented in the chart refers to two-ingredient sprays. If three or more ingredients are mixed, unpredictable incompatibilities may occur. The more materials there are in the tank the greater is the probability of trouble.
- 23. Do not exceed recommended speeds when using a concentrate machine.
- 24. "Semi-concentrate" spraying is more dangerous than concentrate spraying. Contrary to popular opinion "semi-concentrate" spraying, i.e., from 90 to 250 gallons of spray liquid per acre, is

more likely to result in spray injury than true concentrate spraying, i.e., less than 75 gallons per acre, from a similar machine. That is because "semi-concentrate" spraying results in extensive dripping and, with spray materials several times stronger than in gun spraying, injury is likely to occur at the point of drip on leaves or fruits. If a concentrate sprayer is properly designed and adjusted there is no drip at an output of 75 gallons per acre or less.

25. Improper adjustment of concentrate sprayers can cause damage. It is most important that concentrate sprayers have air volume and air velocity adequate to spray the tops of trees without overspraying the bottoms of the trees. Overspraying with a true concentrate sprayer can be recognized by the occurrence of drip. Sometimes overspraying is the result of wrong nozzle arrangement and sometimes of worn orifice discs or swirl plates. Nozzles should be adjusted so that about 75 per cent of the spray liquid is in the upper half of the air stream.

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A Solpugid in British Columbia

A couple of specimens of this near relative of spiders were given me some years ago by a student from southern Alberta. In these animals the head is distinct from the rest of the body and their classification depends upon the teeth in the upper part of the mandibles of the males. On February 14, 1958, Mr. W. Preston, R.R. No. 1, Oliver, in the South of the Okanagan Valley, brought me a solpugid which he had collected in June 1956 near an irrigation ditch. It is a female and so cannot be classified. I think this is the second record of a solpugid being taken in British Columbia. Mr. Jim Grant of Vernon, informed me that Dr. Kurata of the Royal Ontario Museum had reported them some years ago.

-G. J. Spencer, University of British Columbia, Vancouver.