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Soil Research

Supplementary Material

Pesticide extraction from soil into runoff under a rainfall simulator

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Supplemental Material A – Evaluating ‘bulked’ runoff pesticides.

One constraint to studying pesticides runoff is analysis cost. Discharge, sediment load and pesticide runoff concentrations can all change through time. The most useful data are event mean pesticide concentrations. Costs are doubled if samples are filtered and used to determine water and sediment concentrations. In rainfall simulator studies a ‘bulked’ runoff sample taken through the hydrograph was used to determine water and sediment concentrations. Bulked filtered samples provide a flow weighted mean concentration in a single sample, defines whether water or sediment is dominant and allow a partition coefficient to be calculated. Processing filtered samples requires more time between collection and extraction with possible degradation and risk that water or sediment concentrations will be below detection limits, giving a lower total concentration than using total extraction. To check reliability of bulked runoff samples (“bulked”), total concentrations were compared to flow weighted mean concentrations calculated from samples taken through the hydrograph (“runoff”). This will indicate if bulked samples can be used as the primary method for measuring pesticide runoff concentrations.

Methods

Bulked runoff samples were taken by adding a portion of runoff to a single bottle using a constant duration, six times during the hydrograph. Sampling duration was predetermined, based on expected runoff rate, so the sample does not exceed the bottle volume. Pesticide analysis methods are given in the paper. Data from rainfall simulator studies at Emerald and Jondaryan are presented.

Results

Emerald

Bulked runoff concentrations were highly correlated with mean flow weighted total concentrations (Fig. 7). Bulked samples had 27% greater trifluralin concentrations (the deviousness of trifluralin!). Bulked average absolute error was 16.7%, or 12.7% when trifluralin was excluded. Alpha endosulfan was 16% lower in bulked samples than in runoff due to degradation in sediment, a

problem avoided latter. Other bulked pesticides had average concentrations within $\pm 6\%$, average error of -1.5% and average absolute error of 11.7% .

Jondaryan

Bulked and runoff concentrations were highly correlated (Fig. 8). Bulk concentrations were 13% lower than runoff concentrations on average, with an average absolute error of 11.3% ($N=60$). Largest differences were for most recently sprayed plots (BP_5 2d after spraying) where runoff concentrations were 21% higher than bulked (Fig. 9). When BP_5 was excluded, concentrations were within 6% on average (Fig. 8) with an average absolute error of 10.2% ($N=46$). Thus, bulked gave reliable estimates pesticide concentrations, as found by Masters et al., (2013).

Supplemental Material B – Pesticide analysis, Jondaryan

Soil and runoff pesticides analysed by QHSS:

OC's: α -, β -, sulfate-, total endosulfan, metolachlor, pendimethalin, trifluralin, DDE

Herbicides: diuron, fluometuron, prometryn

OP's: profenofos, chlorpyrifos, dimethoate, monocrotophos

Water: Solvent extraction where 60 gm NaCl dissolved in water and extracted with dichloromethane (EPA-Method-3510). Concentrated extracts were quantified using gas chromatography and electron capture detection for OC's, endosulfan, trifluralin, metolachlor and pendimethalin. Quantitation (EPA-8080) for OC's and EPA method 8140 for OP's, using gas chromatography and nitrogen phosphorus detection, also for prometryn. OP's were confirmed using flame photometric detection. Reference for prometryn and trifluralin is EPA method 507. Diuron and fluometuron quantitation used HPLC with UV detection. Column was a Hypersil MOS C8 5micron column and mobile phase with gradient elution using acetonitrile and water.

Sediments: Method AOAC-15th-edition-(1990)-No-970.52M for extraction and quantitation.

Filter papers were analysed using acetone and quantitation as for water.

Detection limits:	<u>Group</u>	<u>Water</u>	<u>Soil</u>
		($\mu\text{g L}^{-1}$)	($\mu\text{g kg}^{-1}$)
	OC	0.1	10
	OP	0.5	10
	Herbicides	0.1	10

References

EPA/600/R-95/131 (1995). Methods for the Determination of Organic Compounds in Drinking

Water. EPA Method 507: Determination of Nitrogen-and Phosphorus-Containing Pesticides in Water by Gas Chromatography with a Nitrogen-Phosphorus detector.

EPA Test Methods for Evaluating Solid Waste (1986). EPA method 3510: Separatory Funnel Liquid-Liquid Extraction.

EPA Test Methods (1996). Method 8081A. Organochlorine pesticides by Gas Chromatography.

EPA Test Methods (1996). Method 8141A. Organophosphorus Compounds by Gas Chromatography: Capillary Column Technique.

Official Methods of Analysis of AOAC International 15th Edition (1990) Method 970.52M: Organochlorine and Organophosphorus Pesticides in Soil.

Supplemental Material C – Pyrethrin sodium analysis

Soil pyrethrin sodium (Jondaryan) analysed by two methods:

- a) GC-MS (Bruns and Tauber 1992, Sumpter et al. 1996) (extraction and cleanup). Pyrethrin sodium was extracted from 10gm soil by Milli-QR water at subcritical conditions (100°C, 2000psi) using a DIONEX ASETM200 Extractor (Accelerated Solvent Extraction, ASE). Pyrethrin was separated from extract using a graphitised carbon column, eluted from the column, and analysed by GC with MS detection. Efficiency was checked by analysing soil fortified with pyrethrin with 2-317 $\mu\text{g kg}^{-1}$. Average recovery was 90%. Detection limit and LOQ were 0.3 and 1.0 $\mu\text{g kg}^{-1}$ (ppb), respectively.
- b) ELISA (Wang *et al.* 1998). Two extractions were used: ASE (Sumpter *et al.* 1996) and PBS (10gm soil shaken overnight with 20mL phosphate-buffered saline and filtered prior to dilution and analysis). Mean (PBS and ASE) concentrations were not significantly different from GC using two-way ANOVA with blocking on log transformed data and were used.

References

- Bruns GW, Tauber R (1992). Determination of KIH-2031 (DPX-PE350) in Soil by Gas Chromatography/Mass Spectrometry. Report No AMR2421-92, DuPont Agricultural Products Experimental Station, Wilmington, Del., USA.
- Sumpter S, Peterson BA, Mulderig LJ, Ledeker KW (1996). Analytical method for the determination of pyrethrin sodium in soil using subcritical water extraction, graphitized carbon cleaned-up, and column-switching LC/UV analysis with confirmation by LC/MS. DuPont Report No AMR 2745-93, Wilmington, Del., USA.
- Wang S, Beasley H, Kennedy IR (1998). Validation of pyrethrin sodium (Staple) ELISA for Australian soils. CRC for Sustainable Cotton Production, University of Sydney, Australia.

Figures for Supplemental Material A

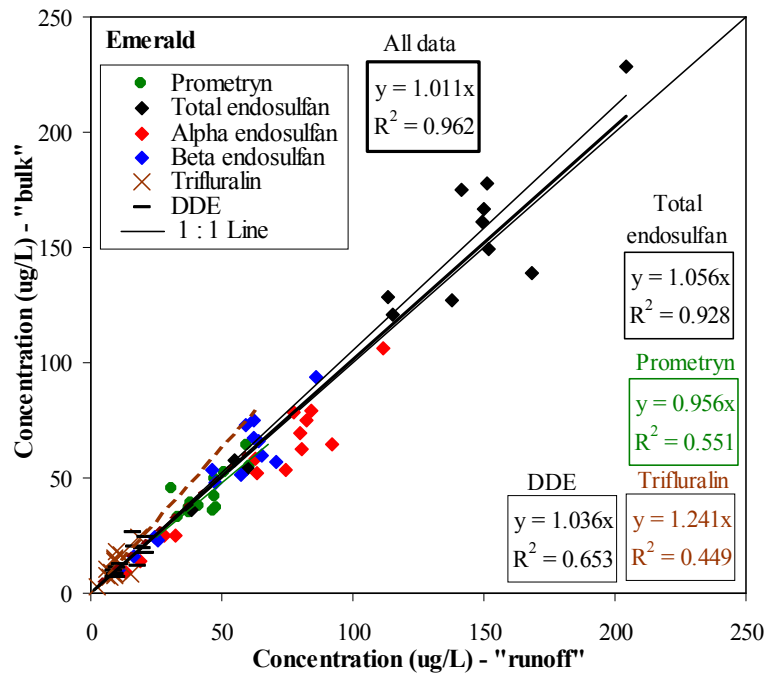


Fig. 7. Bulkied runoff total and flow weight concentrations, Emerald.

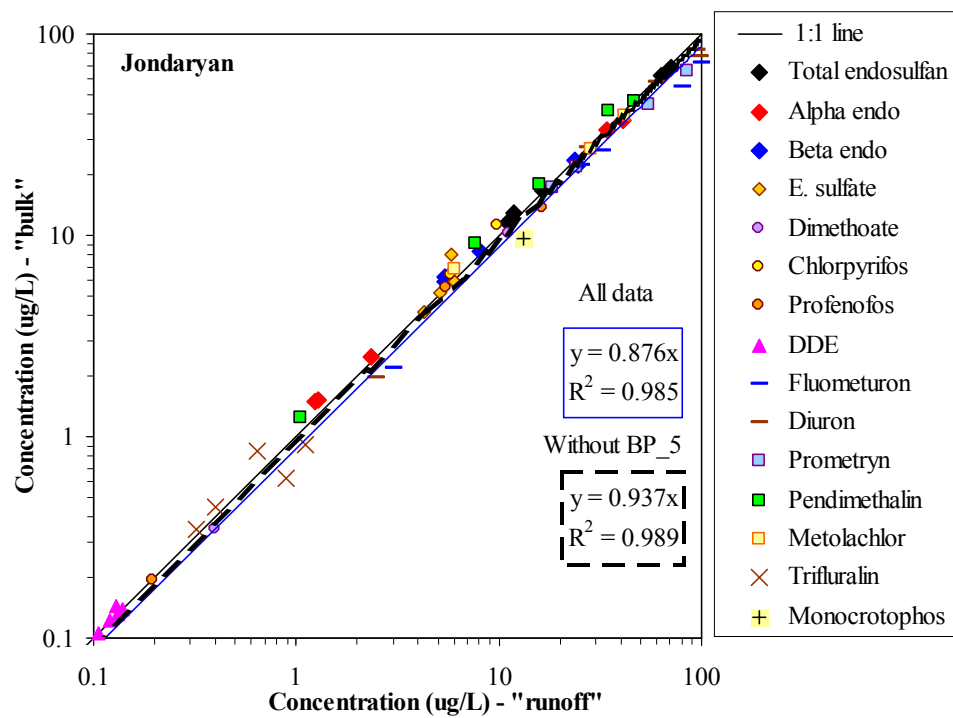


Fig. 8. Bulked runoff total and flow weight concentrations, Jondaryan.

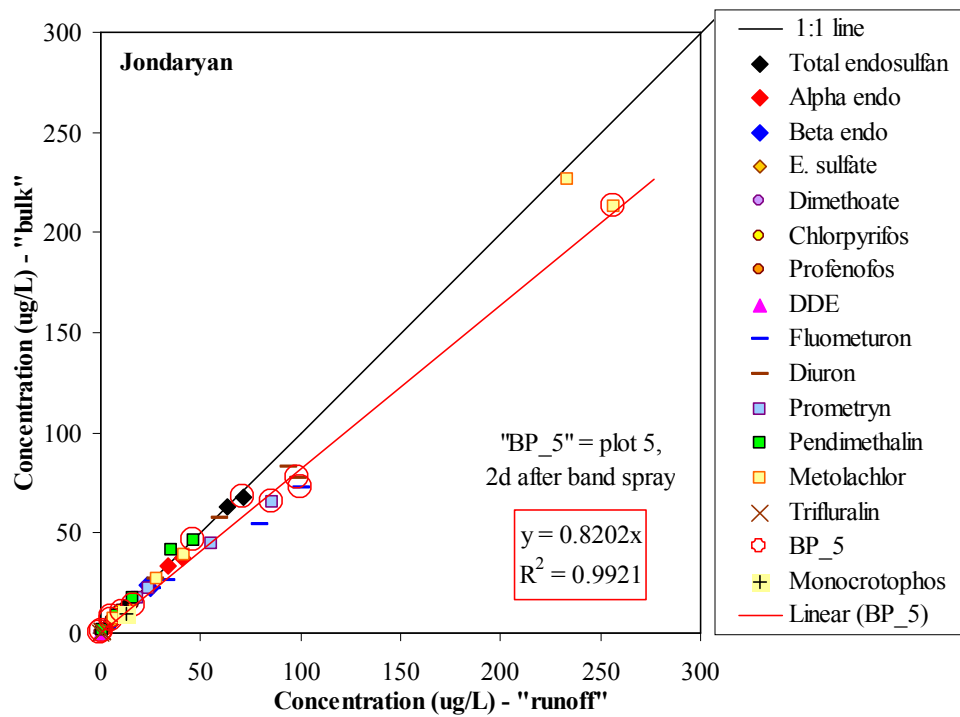


Fig 9. Bulked runoff total and flow weight concentrations, Jondaryan. BP_5 was 2 days after band spraying.