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Diverse effects of wetting and drying cycles on soil aggregation: Implications on pesticide leaching

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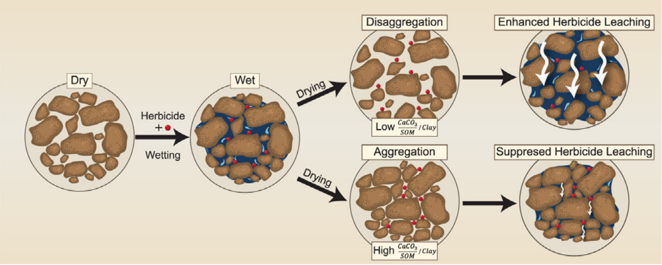
HIGHLIGHTS

- Soil wetting and drying induces micro-changes in aggregate stability.
- $CaCO_3$ and organic matter are key factors in aggregation of clayey soils.
- Soil stabilization, aggregation, may reduce pesticide mobility.
- Soil disaggregation may enhance pesticide mobility.
- Pesticide physical-chemical properties dominate their mobility.

GRAPHICAL ABSTRACT



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ABSTRACT

The important effect of soil wetting and drying cycle (WDC) on soil structure, and the consequent effect on pollutant fate is underexplored. We thoroughly investigated the changes in soil structure and in leaching of Alion (indaziflam) and Express (tribenuron methyl), pre and post WDC, from two clayey soils and two loamy soils under different land uses (uncultivated, field crops, and orchards). Soil stability was quantified by an aggregate durability index we recently developed. WDC did not affect the stability of the sandy-loam soils, as expected. However, for the sandy-clay-loam with high $CaCO_3$ content aggregation was observed. For the clayey soils with similar $CaCO_3$, aggregation and disaggregation were obtained, for a soil with relatively low and high SOM, respectively. The stability trends are reflected by the ratio between the contents of inorganic carbon and soil organic matter (SOM), $CaCO_3$/SOM, normalized to the clay content. Aggregation was explained by $CaCO_3$ cementation, while disaggregation was attributed to high clay content and to alterations in SOM conformation post WDC. These opposite trends, obtained for the two clayey soils, were confirmed by analyzing changes in soil packing employing X-ray tomography (micro-CT). Our results clearly demonstrated that soil aggregation and disaggregation, induced by a WDC, suppresses and enhances herbicide mobility, respectively. However, the effect of WDC on herbicide leaching was not noticeable for Alion upon its high adsorption to a clayey soil, indicating that herbicide physical-chemical properties may dominate. Finally, WDC induces micron-scale changes in aggregate structure, which have a notable effect on pollutant mobility and fate in the environment.

1. Introduction

The conservation and sustainability of soil and water as natural resources are impacted by both natural processes and modern agricultural practices. The use of herbicides in agriculture provides

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substantial agronomic and economic benefits, however, herbicide migration in the environment may pose soil, groundwater and surface water pollution (Gilliom, 2007; Jarvis, 2007; Stehle and Schulz, 2015; Van Der Werf, 1996). It is well-known that the physicochemical properties of the herbicide, and soil characteristics such as texture, pH, organic matter (OM), and mineralogy govern herbicide mobility (Carter, 2000). In addition, many studies have demonstrated the strong impact that tillage and irrigation, and obviously precipitation, have on herbicide fate (Alletto et al., 2010; Isensee; Sadeghi, 1994; Sigua et al., 1993).

However, fewer studies have addressed the complex effects that soil wetting and drying cycles (WDCs) have on herbicide mobility. Soil wetting and drying occurs naturally at different time scales from days, seasons to extreme climate events. Wetting, due to precipitation or irrigation, and drying in the field, are most frequent in semi-arid to arid climates, in which the drying usually occurs within a few days. The few studies that explored the impact of soil wetting and drying on herbicide fate report diverse trends. For example, following a WDC, concentrations of atrazine, diuron, terbuthylazine, and linuron in the soil solution were found to decrease (Haouari et al., 2006; Kottler et al., 2001; Lennartz and Louchart, 2007; Louchart et al., 2005; Shelton and Parkin, 1991). In contrast, others have reported that soil solution concentrations of imazaquin (Baughman and Shaw, 1996), ethidimuron and methabenzthiazuron (Jablonowski et al., 2012) increased following WDC. In many cases, the variability in herbicide concentrations are affected by WDCs and their consequent effect on the microbial activity (Baughman and Shaw, 1996; Shelton and Parkin, 1991).

Recently we have reported the effect of soil wetting and drying on soil structure and the consequent effect on herbicide mobility (Dor et al., 2019; Goldreich et al., 2011). We found that enhanced or suppressed atrazine release and leaching, following a WDC, correlated to soil disaggregation or aggregation of the soil structure, respectively (Dor et al., 2019). Soil structure refers to the packing of the solid particles into an aggregated system composing intra- and intermediate pores (Amézketa, 1999), while soil structural stability is the ability to retain its packing under stress (Amézketa, 1999). Therefore the soil structural strength is measured mainly through the aggregate stability and changes in the pore system (Amézketa, 1999; Bissonnais, 1996; Utomo and Dexter, 1982). In our study we also employed advanced methods to assess soil aggregate packing and stability by measuring changes in the particle size distribution, extracted from micro-CT 3D images, and by developing a soil aggregate durability index (*ADI*), respectively (Dor et al., 2019).

The current study is built on our recent report (Dor et al., 2019), but those results, although novel, led to limiting conclusions since they were based on a relativly small set of variables and observations. Currently, we expand our investigation by including a broader set of soils and land uses, as well as herbicides with different physical-chemical properties which enables to capture the complexity of the phenomena. We explored two soil textures (clayey and loamy), three land uses for each soil (uncultivated, field crops, and orchards), and two herbicides, and studied the effect of WDC on soil structure and the consequent effect on herbicide mobility, by monitoring two herbicides with very different physical-chemical properties. Express (active ingredient - tribenuron methyl) is highly soluble ($2.04\ g * L^{-1}$), has low log K_{ow} (0.78), and is anionic at the soil pH ($pKa = 4.7$). Alion (active ingredient - indaziflam) has a lower solubility ($0.0028\ g * L^{-1}$), higher log $K_{ow} = 2.8$, and is nonionic ($pKb = 3.5$). Express is widely used as a broadleaf post-emergence inhibitor in cereals (mostly wheat, barley, and oat) and other crops. Even though Express has been extensively used and studied over the past three decades, the understanding of the herbicide leaching and fate in the environment is incomplete (Álvarez-Benedí et al., 1998; Arena et al., 2017; Cessna et al., 2010). Alion is a novel pre-emergence herbicide used primarily in orchards, but also in lawns and residential areas. Alion has been recently introduced to the market and therefore only a handful of studies have studied this herbicide.

We hypothesize that herbicide leaching is affected by soil micro-structural changes induced by wetting and drying, nevertheless, the physical-chemical properties of the herbicide may dominant. Therefore, we first studied the effect of WDC on the structure of four soils under different land uses (uncultivated, field crops and orchards) for each soil. In the second section we explored the consequent effect on Express and Alion leaching, and quantified and coupled the leaching to the changes in soil structure. In addition to linking the microstructural changes in the soil to the behavior of the different herbicides, we discuss the broader implications of our results for the fate of pollutants in the environment.

2. Materials and methods

2.1. Materials

Commercial herbicides Alion (indaziflam 500 g active ingredient (ai)/L liquid) and Express (tribenuron methyl 750 g of ai/L liquid) were obtained from Liddor-Chemicals Ltd., Israel and Gadot-Agro, Israel, respectively.

Soils were sampled from 0 to 20 cm depth from four sites representing major agricultural areas in Israel. Ein Harod and Geva clayey soils were sampled from locations in northern Israel situated in a Mediterranean climate zone). Shikmim sandy clay loam and Magen sandy loam soils were sampled from locations in southern Israel situated in an arid climate zone. In each site, samples were collected from three adjacent locations with different land use: uncultivated, field crops, and orchards. All soil samples were air-dried and sieved (<2 mm). Selected physical and chemical properties of the soils, characterized by standard analytical methods (Dane et al., 2002; Loeppert and Suarez, 1996) are presented in Table 1.

2.2. Soil wetting and drying

Air-dried soil samples were placed on top of filter paper (Whatman No. 1) in Buchner funnels located in a controlled climate greenhouse. Wetting of the samples was carried by irrigation with micro-sprinklers with an average drop size of 65 μm (Netafim CoolNet Pro™ 7.5 L hr−1) to avoid the splash effect (Farres, 1987). Soil pore volume was determined by saturating the soil from beneath with a peristaltic pump, at a slow rate of $0.5\ mm\ h^{-1}$. Soil wetting was performed by adding one pore volume (clayey soils 0.56–0.57 v/v, loamy 0.39–0.46 v/v and sandy soils 0.3–0.35 v/v) of water and stopping immediately when leaching was observed. Drying was carried by raising the greenhouse temperature to ~40 °C until the samples returned to their initial air-dried weight, typically 3–4 days.

2.3. Aggregate durability index (ADI)

Soil micro-structural durability was assessed using a recently developed aggregate durability index (ADI) (Dor et al., 2019). To determine aggregate durability, particle-size distributions of soil samples were measured using laser granulometry (Mastersizer, 2000; malvern instruments, UK). Briefly, the durability quantifies as the difference in coarse fraction between water-stable aggregates size distribution, and the disaggregated particle size

Table 1
Soil physical and chemical properties.

Site	Texture	Land Use	Clay (%)	Silt (%)	Sand (%)	SOM (%)	$CaCO_3$ (%)
Geva	Clay	Uncultivated	57.5	15.0	27.5	1.9	13.1
		Orchards	65.0	15.0	20.0	2.3	13.7
		Field crops	62.5	15.0	22.5	2.4	13.9
Ein Harod	Clay	Uncultivated	60.0	15.0	25.0	3.1	7.9
		Orchards	55.0	15.0	30.0	3.1	13.9
		Field crops	60.0	12.5	27.5	2.9	13.4
Shikmim	Sandy clay loam	Uncultivated	22.5	7.5	70.0	1.8	6.1
		Orchards	22.5	7.5	70.0	2.4	9.9
		Field crops	22.5	7.5	70.0	2.5	13.9
Magen	Sandy loam	Uncultivated	15.0	2.5	82.5	1.5	8.2
		Orchards	12.5	2.5	85.0	1.7	1.7
		Field crops	12.5	5	82.5	1.1	5.8

distribution, post sonication, of the same soil sample. The method is described in detail in the supplementary information (Fig. S1 and equation S1)

To evaluate the effect of soil organic matter (SOM) on aggregate durability, a high-SOM soil (Ein Harod; 3.1%) was heated to 350 °C overnight to remove SOM (Schumacher, 2002), followed by ADI assessment for the reduced SOM samples pre and post WDC.

2.4. Soil microstructure imaging

Ein Harod and Geva soils (~1.8 g, 1–2 mm air-dried), were packed into polycarbonate tubes (6 × 400 mm). Each soil sample was scanned two times, pre and post WDC. Wetting of the soil sample was carried by slowly saturating the soil with distilled water using pipette. Samples were dried in an oven at 40 °C until the samples reached their original air-dried weight.

The soil samples were scanned using a micro CT scanner (Skyscan 1174, Bruker, Belgium). The X-ray source was set at 50 kV and 800 μA. A total of 900 projections were obtained for each sample with an exposure time of 3000 ms and an isotropic voxel size of 9.6 μm. All scans were performed using 0.25 mm Aluminum filter. The NRecon software (NRecon® Skyscan® software, version 1.6.1.2, Bruker, Belgium) was used to reconstruct the X-ray projections into a 16-bit grayscale tiff stack.

3D image processing was carried out by Avizo® software (Thermo Fisher Scientific, USA). A 3D median filter with a neighborhood of 26 voxels was applied over the scan to reduce noise. The solid phase (soil particles) was segmented by thresholding the intensity range. Separation of the soil particles was achieved by applying Avizo built-in *separate objects* module which computes watershed lines on a chamfer distance map in which the intensity represents the minimal distance in voxels from the object boundary. Finally, the separated soil particles volumes were calculated, and their probability density function was estimated using a kernel distribution. Changes in particle size distributions were quantified by subtracting the pre from post WDC curves. The intersection of both distributions (control and wetting and drying) was used to determine a coarse fraction threshold, enabling to quantify the aggregation or disaggregation processes for a given soil.

2.5. Herbicide adsorption on soils

Adsorption isotherms of Alion and Express to the four soils (Table 1) were obtained in batch experiments in triplicates (Dor et al., 2019; Goldreich et al., 2011). Sodium azide (100 mg L^{-1}) was added to the herbicide stock solutionss to inhibit microbial degradation during the adsorption experiment.

Alion or Express, (0.5, 2, 5, 10, and 15 mg a. i. L^{-1} in 20 mL deionized water) were added to soil (8 g) in centrifuge tubes, reaching a soil suspension of 400 g soil L^{-1}. The samples were agitated on a shaker at 25 °C for 48 h, reaching equilibrium. The supernatants were separated by centrifugation at 15,000×*g* for 10 min, filtered with a 0.45-μm pore diameter polytetrafluoroethylene filter, and the active ingredients concentration was measured using HPLC (Agilent 1200 series, Agilent technologies, USA). The HPLC is equipped with a diode-array detector ($\lambda = 222$ nm) and RP-18 column (Waters, Symmerly Shield 3.5 μm, 150 mm). For the analysis of indaziflam, the mobile phase was acetonitrile/0.05% formic acid 45/55 v/v, with a flow rate of 0.75 mL min^{-1} at 25 °C. For the analysis of tribenuron methyl, the mobile phase was acetonitrile/0.05% formic acid 40/60 v/v, flow rate of 1 mL min^{-1} at 25 °C. Freundlich coefficients were deduced from the adsorption isotherms relating the herbicide concentration adsorbed to the surface, C_{ads} (mg kg^{-1}), to the concentration in the solution, C_{eq} (mg L^{-1}), as follows: $C_{ads} = K_f \times C_{eq}^n$, where K_f is the adsorption coefficient and n is the correction factor.

2.6. Herbicide release and leaching through the soil

To simulate leaching of the herbicides through soil, all soil samples (160 g) were placed on a paper filter (Whatman No.1) in a Buchner funnel forming a layer of ~2 cm. The soil samples were subjected to one WDC as described above and then the herbicide was applied. Control samples for each soil were not subjected to this process. The commercial formulations of Express and Alion were applied (0.3 g/m^2) to the soil. Relatively high herbicides doses, with respect to field application, were applied using a nozzle syringe to enable high-performance liquid chromatography (HPLC) analysis; however, previous studies show that the trends obtained from such an experiment predict the leaching trend at field recommended doses (Katz and Mishael, 2014). Alion and Express were applied to the uncultivated soil samples and were applied on orchard and field crop soils, respectively, corresponding to the common agricultural uses of each herbicide. Leaching from the sandy loam soil was not measured due to low herbicide adsorption to this soil. On the other hand, due to the very high adsorption of Alion to both clayey soils, its leaching was studied from one of them, Ein-Harod. The soil samples were then irrigated by adding doses of 40 mL of tap water every 10 min, through a paper filter to maximize irrigation homogeneity, reaching at least five pore volumes (~0.45 L for the clayey soils, ~0.3 L for the loamy and ~0.25 L for the sandy soils). Alion and Express concentrations in all leachates after each irrigation dose were measured as described above.

2.7. Statistical analysis

The significance of the ADI results was tested using a three-way ANOVA for soil type, land use, and WDC as fixed effects. Post hoc slice test was performed on significant effects. The effect of reduced SOM and WDC on ADI in a clayey soil was assessed by a two-way ANOVA test followed by a post hoc slice test. In order to examine the effect of soil WDC on herbicide leaching, a two-way ANOVA was performed on the effect of soil texture and WDC on cumulative amount of herbicide leached after five pore volumes, followed by a post hoc Tukey test. All of the statistical analysis was carried by JMP®, Version 14. SAS Institute Inc.

3. Results and discussion

3.1. Effect of wetting and drying on soil aggregate stability

Soil aggregate stability and packing were assessed by measuring changes in particle-size distribution, using a soil Aggregate Durability Index (ADI) (Dor et al., 2019) and analyzing micro-CT 3D images, respectively. The clayey soils, Ein Harod and Geva, had high ADI values (0.517–0.717) indicating high primarily aggregate stability. Shikmim, a sandy clay loam soil, had intermediate ADI values (0.022–0.149), and Magen, a sandy loam soil, had very low ADI values (0.003–0.02). The calculated ADI values of all soils (Fig. 1a) positively correlated with the percent of silt and clay ($R^2 = 0.97$), (Fig. S2). These results are consistent with previous studies that report a positive correlation between aggregate stability and clay content (Amézketa, 1999).

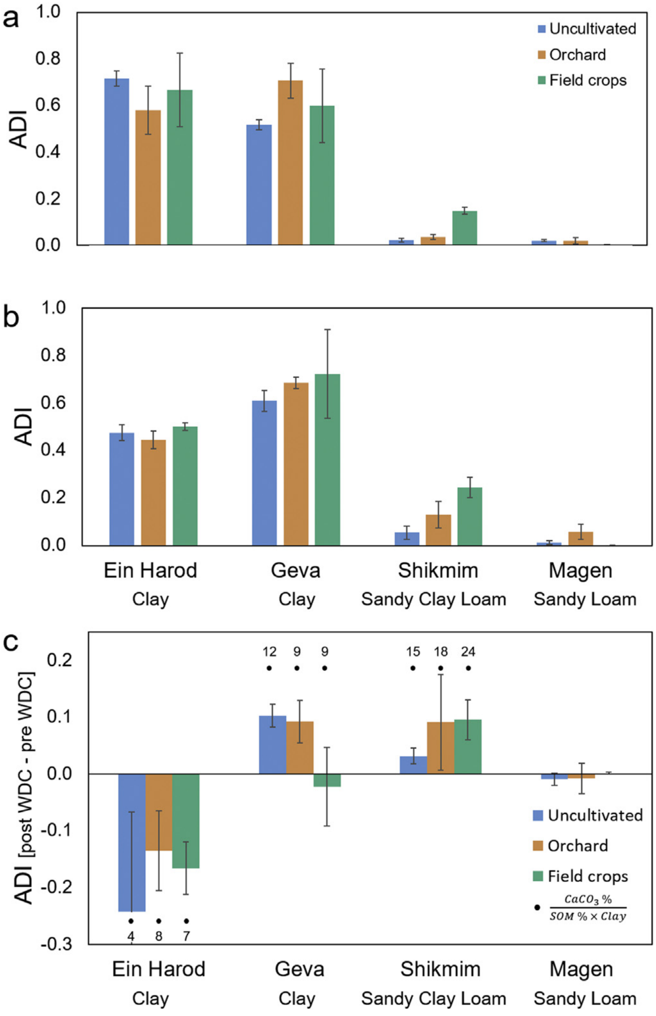

Fig. 1. Aggregate durability index (ADI) values (a) pre wetting and drying and (b) post wetting and drying. (c) Differences in ADI values (bars) (ADI [postWDC-preWDC]), adjusted to $CaCO_3$/SOM ratio and normalized to clay content (dots).

Many reports indicate that intensive soil cultivation leads to a decline in soil structure (Saha and Kukal, 2015; Six et al., 2000); however, there were no significant differences in the ADI values obtained for the different land uses (uncultivated, field crops and orchards) ($p = 0.93$, Table S1), for a given soil. In the current study, we focused on the micro-to macro-aggregates.

The ADI values of the soils were then measured post a WDC (Fig. 1b). As expected, for Magen sandy loam soil, a WDC did not affect soil structure, and indeed the ADI values did not change significantly ($p = 0.378$). However, in Shikmim sandy clay loam, there was a significant increase in the ADI values post WDC ($p = 0.041$) (Fig. 1c). An increase in stability may be explained by dissolution and recrystallization of carbonate minerals upon soil wetting and drying, respectively. We suggest that this phenomenon is most evident at high $CaCO_3$ content (6%–14%) and induces calcite cementation, contributing to the formation of durable aggregates (Boix-Fayos et al., 2001; Dor et al., 2019; Klute et al., 1986; Sposito, 2008). The ADI values after WDC in the Shikmim soils positively correlated with $CaCO_3$ content.

In the clayey soils, Geva and Ein Harod, our hypothesis was that a WDC would induce disaggregation as reported for clayey soils (Dor et al., 2019; Goldreich et al., 2011). Surprisingly, opposite trends were observed; for Ein Harod soils the trend was as expected, with a significant decrease of ~0.2 in the ADI values ($p < 0.0005$), while for the Geva soils, an increase of ~0.1 ($p < 0.0004$) was observed (Fig. 1c). The texture of Ein Harod and Geva soils is rather similar, but there is a slight difference in the soil organic matter (SOM) and $CaCO_3$ contents (Table 1). We propose that there is a correlation between the inorganic and organic carbon ratio, presented as $CaCO_3$/SOM and the opposite stability trends. To account for the different texture of the loamy soil, the ratio is normalized to clay content (i.e. $\frac{CaCO_3}{SOM \times Clay}$). Indeed, the ratio is lower for the Ein Harod soils, (4.2–8.2) than for the Geva soils (9.2–12.0) and for the loamy soil (15.1–23.7). Moreover, our previous study, in which we report an increase and decrease in soil stability for loamy and clayey soils, corresponds to high (30) and low (4.5) $\frac{CaCO_3}{SOM \times Clay}$ values.

It is well known that even small amount of the SOMinduces soil aggregation (Jozefaciuk and Czachor, 2014; Tisdall and Oades, 1982). Indeed, Ein Harod soils that were heated to 350 °C (Schumacher, 2002) to reduce their SOM content had significantly lower ADI values than non-heated soils ($p < 0.0001$, Fig. 2, Table S2). During wetting, the structure and properties of SOM are altered in a complex manner, the SOM does not return to its initial configuration, and therefore aggregate stability may decrease post drying

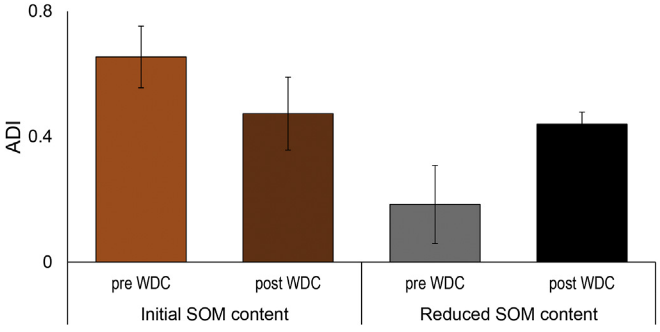

Fig. 2. Aggregate durability index (ADI) values for Ein Harod clayey soil pre and post wetting and drying, with the initial soil organic matter (SOM) content (left) and reduced SOM content (right) by heating the soil to 350 °C.

(Lundquist et al., 1999). For example, it has been reported that for California soils undergoing wetting and drying, the amount of dissolved organic matter increased by about 70%, compared to soils that did not undergo wetting and drying cycles (Lundquist et al., 1999). In addition, after a WDC, the stability of macroaggregates with high SOM decreased, compared to macroaggregates with low SOM whose stability did not change (Denef et al., 2001).

As mentioned above for loamy soils (Shikmim), $CaCO_3$ induces cementation contributing to the formation of durable aggregates. We suggest that high $CaCO_3$ contents will moderate the decrease in aggregate stability post WDC caused by the effect of SOM, and in some cases result in an increase in aggregate stability, as seen in the case of Geva clay soil. Also, in the case of the Ein Harod soil in which the SOM content was reduced, an increase in aggregate stability post WDC was observed (Fig. 2), in contrast to the decrease observed in the untreated soil (Fig. 1b). These results emphasize that SOM has a complex effect on aggregate stability and soil structure.

3.2. *Effect of wetting and drying on soil packing*

To further characterize the opposite stability trends of wetting and drying on the structure of clayey soils, we imaged aggregate packing by analyzing micro CT images pre and post WDC. Particle size distribution curves were extracted from the micro CT scans by image processing techniques (see methods 2.4), and the probability density function was fitted to each distribution. Ein Harod soil particle size distribution shifted to smaller particle sizes post a WDC (Fig. 3a). A lager fraction of small particle indicates disaggregation. In contrast, Geva soil particle size distribution shifted to larger particle sizes indicating aggregation (Fig. 3b). These shifts in particle size distributions were quantified by subtracting the pre from post WDC curves (Fig. 3c and d). A loss of ~15% and a gain of ~23% in the coarse fraction for Ein Harod and Geva soils was obtained, respectively. The soil packing analysis supports the surprising opposite soil stability trends obtained for the clayey soils.

3.3. *Alion and Express adsorption to soils*

The adsorption of Alion and Express to the soils was determined (Fig. S3 and Fig. 4) and their leaching from the soils was studied, pre and post WDC, to establish the link between soil aggregate stability and herbicide leaching. The adsorption isotherms of Alion and Express (0.5–15 mg L^{-1}) to the soils (Table 1) were obtained (Fig. S3) and Freundlich coefficients were calculated (Table S3). The adsorption isotherms are of type C ($n \cong 1$) (Sposito, 2008), suggesting that adsorption followed a partition-like trend and the K_d coefficients are presented (Fig. 4). No significant differences in herbicide adsorption (K_d) were observed for the different land uses for a given soil ($p > 0.1$; Tables S4–S5).

The adsorption of Alion was higher than Express in all cases due to its physical-chemical properties. Express has high solubility (2.04 g L^{-1}), low log K_{ow} (0.78) and is anionic at the soil pH ($pK_a = 4.7$), while Alion has a lower solubility (0.0028 g L^{-1}), higher log $K_{ow} = 2.8$ and is nonionic ($pK_b = 3.5$). The effect of a compound's charge on its leaching is well established (Carter, 2000; Flury, 1996). Leaching is more pronounced in anionic compounds, such as Express, compared to nonionic compounds, such as Alion, mainly due to the inherently negatively charged soil clay-mineral (Flury, 1996). The solubility of herbicides is another well-known factor that govern herbicide leaching. As compound solubility increases, its tendency for transport increases (Carter, 2000). Only a few studies measured the adsorption of Alion to soils, and medium to high adsorption ($K_d = 5.2$–27.4 L kg^{-1}, and $1/n \cong 1$) was reported, with an increase in adsorption as the content of SOM and clay increases (Alonso et al., 2011; González-Delgado et al., 2015). In the current study, similar trends were obtained with very high ($K_d = 8.4$–13.1 L kg^{-1}) and low ($K_d = 0.8$–5.2 L kg^{-1}) adsorption to clayey and loamy soils, respectively. Express adsorption was considerably lower than Alion to all soils, with less pronounced differences between the clayey and sandy soils. The high adsorption of Alion led to low concentrations measured in the supernatant, and result in larger standard deviations in its calculated K_d values. As reported in the literature, the adsorption of Express to soils is low to moderate (Álvarez-Benedí et al., 1998; Cessna et al., 2010).

3.4. *Effect of wetting and drying on herbicide leaching*

Herbicide leaching (pre WDC) through a thin soil layer was studied by measuring its concentrations in the leachates of five consecutive soil pore volumes. The cumulative herbicide leaching as a function of pore volumes is presented in Fig. 5. Alion and Express leaching was tested on soil from land uses that correspond to the common agricultural use of each herbicides (see section 2.6). The leaching trends are in agreement with the adsorption characteristics. Higher leaching of Express compared to Alion and higher leaching from the loamy soils compared to the clayey soils.

Herbicide leaching from the soils were also measured post a WDC (Fig. 5). Leaching of Express from the Shikmim sandy clay loam soil was nearly complete pre and post WDC (Fig. S4a), which is in agreement with previous results reported for a sandy clay loam soil (Cessna et al., 2010; Kotoula-Syka et al., 1993). WDC induced aggregation of Shikmim sandy clay loam soil (Fig. 1). However, these changes in soil structure did not affect Express cumulative leaching since there is minimal interaction between the herbicide and the soil particles. Yet, although Express leaching was nearly 100% of the adsorbed amount, the observed differences in the leaching rate pre and post WDC imply on the soil structural changes. In contrast to Express, Alion leaching from the sandy clay loam soil was suppressed significantly ($p < 0.0001$) post WDC (20% leaching vs. 40% for the control soil), due to soil aggregation, which may 'trap' the herbicide and 'shield' it from the soil solution (Fig. 5a).

For the clayey soils, Alion leaching pre and post WDC did not differ significantly ($p = 0.6$, Fig. S4b), despite the changes in soil structure, since Alion adsorption is so high and its leaching restricted (Fig. 5d). The observed high adsorption of Alion is in agreement with the low mobility potential reported from six soils varying in their physical-chemical properties (Alonso et al., 2011). Additionally, bioassays for Alion leaching reported limited leaching in a sandy soil (Jhala and Singh, 2012) and very low leaching potential in clayey soils (Guerra et al., 2016). In the case of Express leaching, pre and post WDC, we observed two opposing trends. Cumulative leaching of Express from the Geva soil post WDC was significantly suppressed compared to the control soils (65% vs. 75%, $p = 0.0018$) (Fig. 5b and e). On the other hand, for Ein Harod we observed a significant ($p < 0.001$) increase in Express leaching, with 85% vs. 65% leaching from the control soil (Fig. 5c and e). These opposite trends are in agreement with the post WDC aggregation and disaggregation of Geva and Ein Harod, respectively (Fig. 1). Upon a WDC, soils which undergo disaggregation may release physically trapped herbicides and expose soil surfaces to the soil solution, inducing herbicide release. In contrast, soil aggregation may entrap herbicides and reduce their exposure to soil solution and their release (Fig. 6).

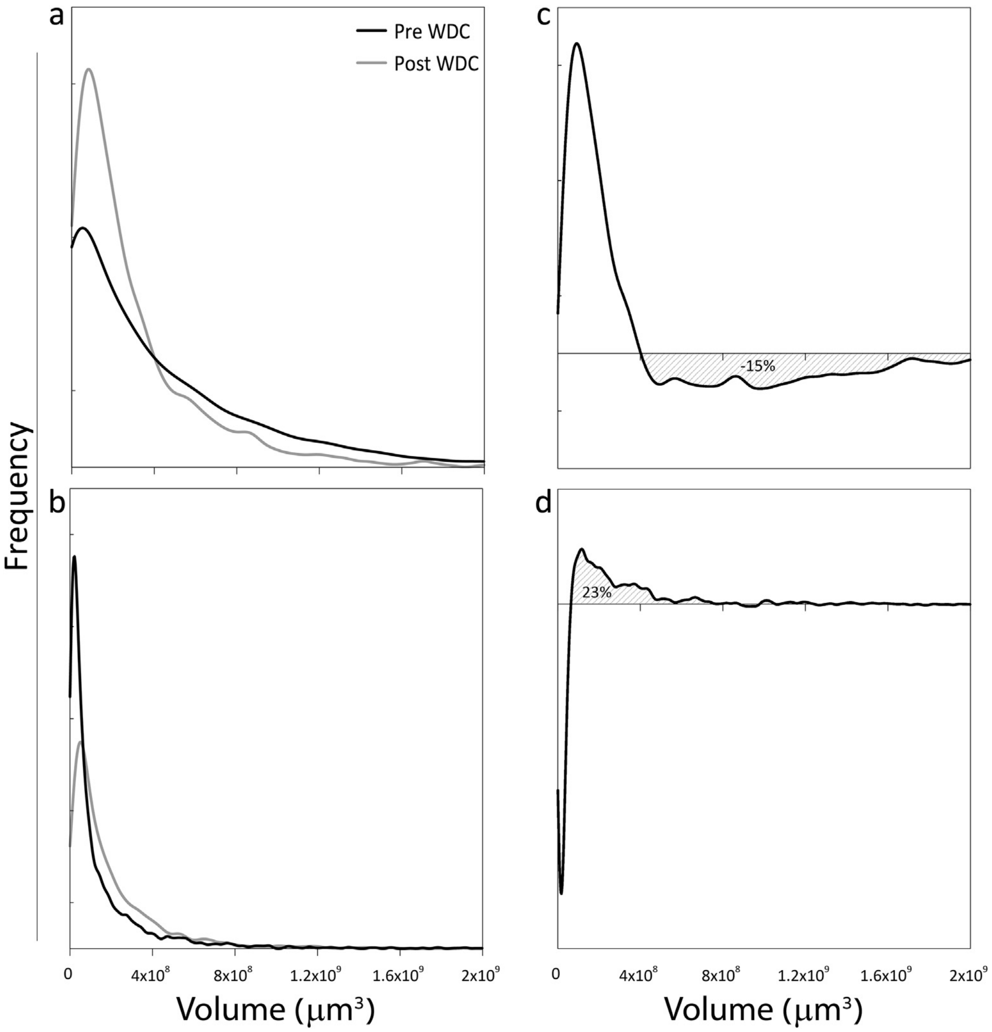

Fig. 3. Particle size distribution of Ein Harod (a) and Geva (b) pre and post a wetting and drying cycle. Subtraction of the control from post wetting and drying curves for Ein Harod (c) and Geva (d) soils, highlighting the effect on the larger particle size of each soil.

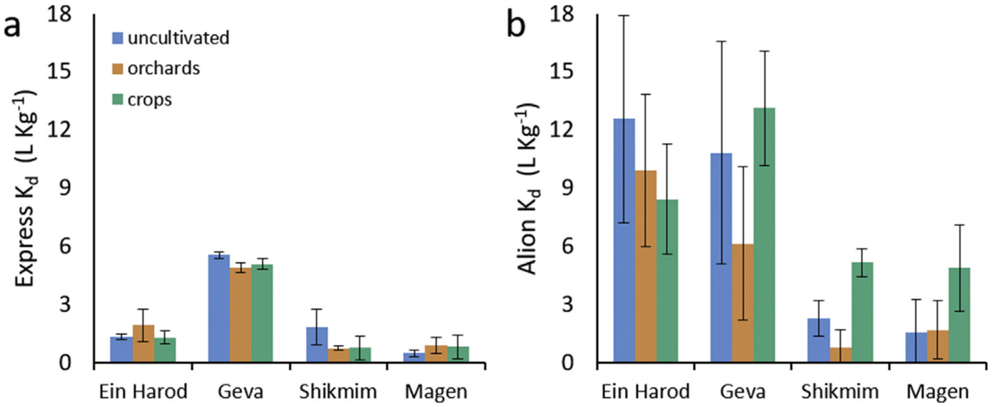

Fig. 4. Adsorption coefficients (K_d) of Express (a) and Alion (b) to the different soils. For any given soil, the K_d values are not significantly different for the three land uses, uncultivated, orchards and crops.

4. Conclusions

To conclude, we analyzed and quantified the effect of WDC on structural changes and herbicide leaching of two herbicides, Express and Alion, in four soils. For each soil we sampled three adjacent sites with different land uses: uncultivated, field crops, and orchards. Land uses had little effect on soil stability, as well as on herbicide leaching. Our results clearly demonstrate that soil aggregation and disaggregation, induced by a WDC, suppresses and enhances herbicide mobility, respectively. Upon a WDC, Ein Harod

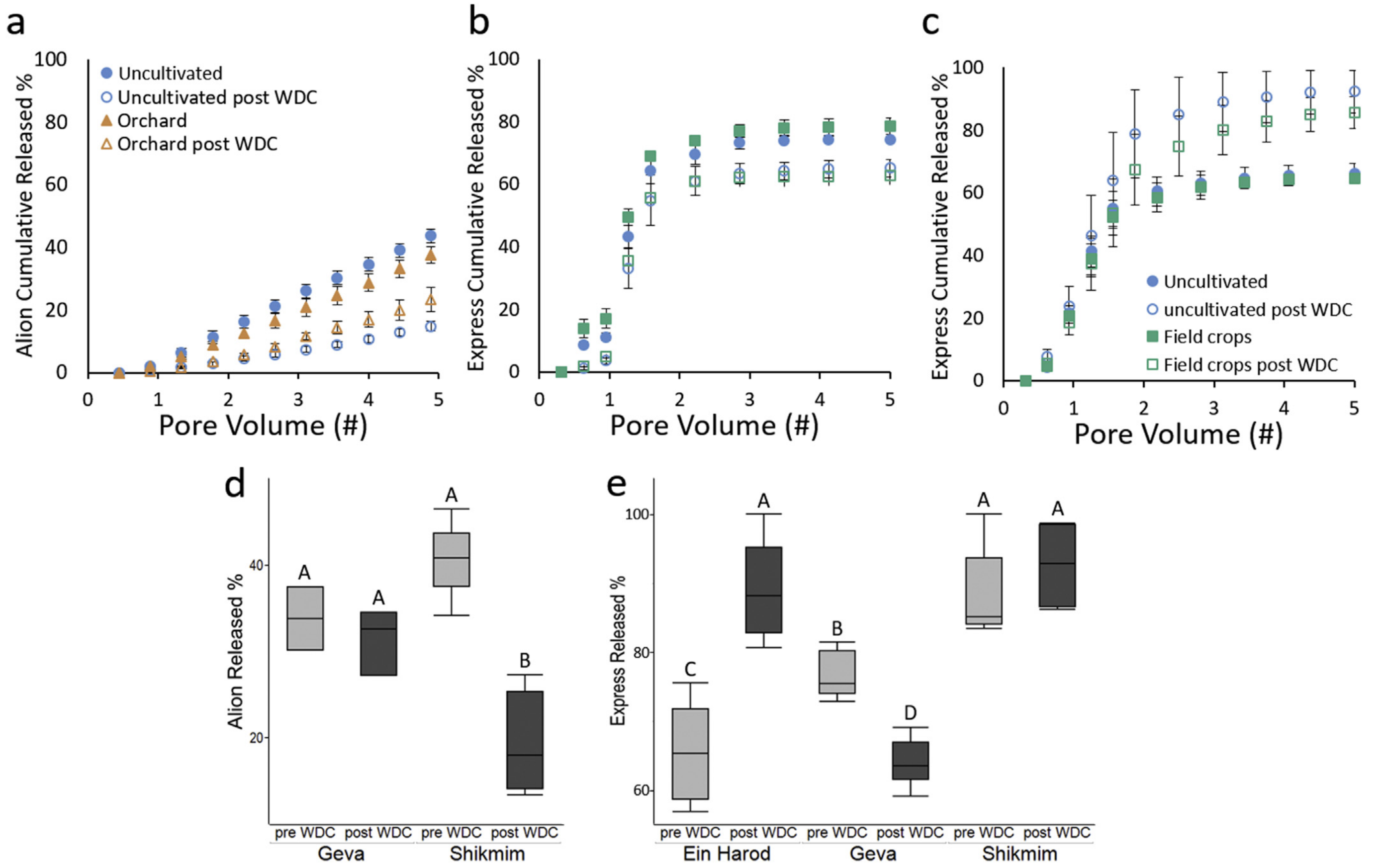

Fig. 5. Alion leaching through a thin soil layer in Shikmim sandy clay loam (a). Express leaching in Geva Clay (b) and Ein Harod clay (c). Alion (d) and Express (e) cumulative leaching after 5 pore volumes in soils. Different letters signify significant differences.

clay soil structure weakened, whereas the structure of Geva clay and Shikmim sandy clay loam soils strengthened, due to $CaCO_3$ cementation. Since $CaCO_3$ strengthens soil stability, while alterations in SOM confirmation may weaken soil structure, we proposed and showed that for soils with a similar texture, $CaCO_3$/SOM will determine the stability trend. These trends are in agreement with the assessment of soil packing by micro-CT images obtained for the clayey soil.

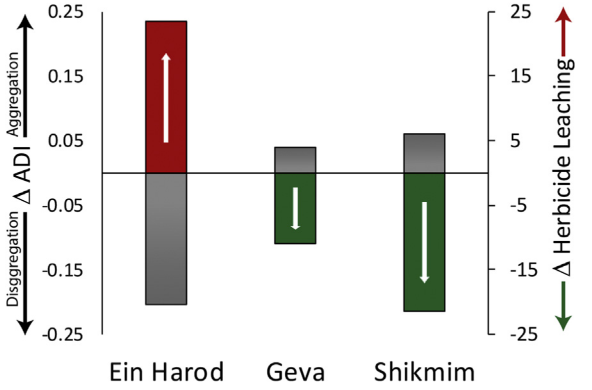

Fig. 6. Soil aggregation induced by wetting and drying reduces herbicide leaching (in green), while disaggregation enhances leaching (in red). White arrows indicate direction of leaching. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Although WDC induced soil aggregation and disaggregation followed by the corresponding leaching trends, herbicide properties may dominate its leaching. For example, Alion adsorption to the clayey soils was very high (~84% from initial concentration), its leaching extremely low (~20%). Thus the effect of WDC was not noticeable.

Our study emphasizes the importance and complex effects of WDC on herbicides leaching since soil texture, SOM and $CaCO_3$ content and herbicide properties all have an effect. Additional parameters such as soil solution (salinity and pH), redox potential, microbial activity, plants, water quality, irrigation practices and precipitation variability etc., should be explored as well. Furthermore, the effect of WDC on herbicide desorption kinetics and leaching rate, invites further research. Finally, wetting and drying directly affects the soil micro-structure which has an immense indirect effect on pollutant mobility, with both reducing soil and water quality from an agriculture and an environmental perspective. Moreover, climate changes will expose a larger part of earth to extreme climatic conditions emphasizing the importance of better understanding the effect of the intensity and frequency of WDCs.

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Declaration of competing interest

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2020.127910.

References

Alletto, L., Coquet, Y., Benoit, P., Heddadj, D., Barriuso, E., 2010. Tillage management effects on pesticide fate in soils. A review. Agron. Sustain. Dev. 30, 367–400. https://doi.org/10.1051/agro/2009018.

Alonso, D.G., Koskinen, W.C., Oliveira, R.S., Constantin, J., Mislankar, S., 2011. Sorption–desorption of indaziflam in selected agricultural soils. J. Agric. Food Chem. 59, 13096–13101. https://doi.org/10.1021/jf203014g.

Álvarez-Benedí, J., Cartón, A., Fernández, J.C., 1998. Sorption of tribenuron-methyl, chlorsulfuron, and imazamethabenz-methyl by soils. J. Agric. Food Chem. 46, 2840–2844. https://doi.org/10.1021/jf970710x.

Amézketa, E., 1999. Soil aggregate stability: a review. J. Sustain. Agric. 14, 83–151. https://doi.org/10.1300/J064v14n02_08.

Arena, M., Auteri, D., Barmaz, S., Bellisai, G., Brancato, A., Brocca, D., Bura, L., Byers, H., Chiusolo, A., Court Marques, D., Crivellente, F., De Lentdecker, C., De Maglie, M., Egsmose, M., Erdos, Z., Fait, G., Ferreira, L., Goumenou, M., Greco, L., Ippolito, A., Istace, F., Jarrah, S., Kardassi, D., Leuschner, R., Lythgo, C., Magrans, J.O., Medina, P., Miron, I., Molnar, T., Nougadere, A., Padovani, L., Parra Morte, J.M., Pedersen, R., Reich, H., Sacchi, A., Santos, M., Serafimova, R., Sharp, R., Stanek, A., Streissl, F., Sturma, J., Szentes, C., Tarazona, J., Terron, A., Theobald, A., Vagenende, B., Verani, A., Villamar-Bouza, L., Villamar-Bouza, L., 2017. Peer review of the pesticide risk assessment of the active substance tribenuron-methyl. EFSA J 15. https://doi.org/10.2903/j.efsa.2017.4912.

Baughman, T., Shaw, D., 1996. Effect of wetting/drying cycles on dissipation patterns of bioavailable imazaquin. Weed Sci. 44, 380–382.

Bissonnais, Y., 1996. Aggregate stability and assessment of soil crustability and erodibility: I. Theory and methodology. Eur. J. Soil Sci. 47, 425–437. https://doi.org/10.1111/j.1365-2389.1996.tb01843.x.

Boix Fayos, C., Calvo Cases, A., Imeson, A., Soriano Soto, M., 2001. Influence of soil properties on the aggregation of some Mediterranean soils and the use of aggregate size and stability as land degradation indicators. Catena 44, 47–67. https://doi.org/10.1016/S0341-8162(00)00176-4.

Carter, 2000. Herbicide movement in soils: principles, pathways and processes. Weed Res. 40, 113–122. https://doi.org/10.1046/j.1365-3180.2000.00157.x.

Cessna, A.J., Elliott, J.A., Bailey, J., 2010. Leaching of three sulfonylurea herbicides during sprinkler irrigation. J. Environ. Qual. 39, 365–374. https://doi.org/10.2134/jeq2008.0497.

Dane, J.H., Topp, C.G., Gee, G.W., Or, D., 2002. 2.4 particle-size analysis. In: Methods of Soil Analysis, vol. 4, pp. 255–293. https://doi.org/10.2136/sssabookser5.4.c12.

Denef, K., Six, J., Paustian, K., Merckx, R., 2001. Importance of macroaggregate dynamics in controlling soil carbon stabilization: short-term effects of physical disturbance induced by dry–wet cycles. Soil Biol. Biochem. 33, 2145–2153. https://doi.org/10.1016/S0038-0717(01)00153-5.

Dor, M., Emmanuel, S., Brumfeld, V., Levy, G.J., Mishael, Y.G., 2019. Microstructural changes in soils induced by wetting and drying: effects on atrazine mobility. Land Degrad. Dev. 30, 746–755. https://doi.org/10.1002/ldr.3256.

Farres, P.J., 1987. The dynamics of rainsplash erosion and the role of soil aggregate stability. Catena 14, 119–130. https://doi.org/10.1016/S0341-8162(87)80009-7.

Flury, M., 1996. Experimental evidence of transport of pesticides through field soils—a review. J. Environ. Qual. 25, 25–45. https://doi.org/10.2134/jeq1996.00472425002500010005x.

Gilliom, R.J., 2007. Pesticides in U.S. Streams and groundwater. Environ. Sci. Technol. 41, 3408–3414. https://doi.org/10.1021/es072531u.

Goldreich, O., Goldwasser, Y., Mishael, Y.G., 2011. Effect of soil wetting and drying cycles on metolachlor fate in soil applied as a commercial or controlled-release formulation. J. Agric. Food Chem. 59, 645–653. https://doi.org/10.1021/jf102960g.

González-Delgado, A.M., Ashigh, J., Shukla, M.K., Perkins, R., 2015. Mobility of indaziflam influenced by soil properties in a semi-arid area. PloS One 10, e0126100. https://doi.org/10.1371/journal.pone.0126100.

Guerra, N., Oliveira Júnior, R.S., Constantin, J., Oliveira Neto, A.M., Gemelli, A., Pereira Júnior, D.M., Guerra, A., 2016. Persistence of biological activity and leaching potential of herbicides aminocyclopyrachlor and indaziflam in soils with different Textures1. Planta Daninha 34, 345–356. https://doi.org/10.1590/S0100-83582016340200016.

Haouari, J., Dahchour, A., Peña-heras, A., Louchard, X., Lennartz, B., Alaoui, M., Satrallah, A., 2006. Behavior of two phenyl urea herbicides in clayey soils and effect of alternating dry-wet conditions on their availability. J. Environ. Sci. Health Part B Pestic. Food Contam. Agric. Wastes 41, 883–893. https://doi.org/10.1080/03601230600805980.

Isensee, A., Sadeghi, A., 1994. Effects of tillage and rainfall on atrazine residue levels in soil. Weed Sci. 42, 462–467. https://doi.org/10.1017/S0043174500076773.

Jablonowski, N.D., Linden, A., Köppchen, S., Thiele, B., Hofmann, D., Burauel, P., 2012. Dry-wet cycles increase pesticide residue release from soil. Environ. Toxicol. Chem. 31, 1941–1947. https://doi.org/10.1002/etc.1851.

Jarvis, N.J., 2007. A review of non-equilibrium water flow and solute transport in soil macropores: principles, controlling factors and consequences for water quality. Eur. J. Soil Sci. 58, 523–546. https://doi.org/10.1111/j.1365-2389.2007.00915.x.

Jhala, A.J., Singh, M., 2012. Leaching of indaziflam compared with residual herbicides commonly used in Florida citrus. Weed Technol. 26, 602–607. https://doi.org/10.1614/wt-d-11-00161.1.

Jozefaciuk, G., Czachor, H., 2014. Impact of organic matter, iron oxides, alumina, silica and drying on mechanical and water stability of artificial soil aggregates. Assessment of new method to study water stability. Geoderma 1–10. https://doi.org/10.1016/J.GEODERMA.2014.01.020, 221–222.

Katz, H., Mishael, Y.G., 2014. Reduced herbicide leaching by in situ adsorption of herbicide–micelle formulations to soils. J. Agric. Food Chem. 62, 50–57. https://doi.org/10.1021/jf403456m.

Klute, A., Kemper, W.D., Rosenau, R.C., 1986. Aggregate stability and size distribution. In: Methods of Soil Analysis, Part 1 - Physical and Mineralogical Methods, pp. 425–442. https://doi.org/10.2136/sssabookser5.1.2ed.c17.

Kotoula-Syka, E., Eleftherohorinos, I.G., Gagianas, A.A., Sficas, A.G., 1993. Phytotoxicity and persistence of chlorsulfuron, metsulfuron-methyl, triasulfuron and tribenuron-methyl in three soils. Weed Res. 33, 355–367. https://doi.org/10.1111/j.1365-3180.1993.tb01951.x.

Kottler, B.D., White, J.C., Kelsey, J.W., 2001. Influence of soil moisture on the sequestration of organic compounds in soil. Chemosphere 42, 893–898. https://doi.org/10.1016/S0045-6535(00)00194-6.

Lennartz, B., Louchart, X., 2007. Effect of drying on the desorption of diuron and terbuthylazine from natural soils. Environ. Pollut. 146, 180–187. https://doi.org/10.1016/j.envpol.2006.04.040.

Loeppert, R.H., Suarez, D.L., 1996. Carbonate and Gypsum. https://doi.org/10.2136/sssabookser5.3.c15.

Louchart, X., Lennartz, B., Voltz, M., 2005. Sorption behaviour of diuron under a mediterranean climate. Agron. Sustain. Dev. 25, 301–307. https://doi.org/10.1051/agro:2005008.

Lundquist, E., Jackson, L., Scow, K., 1999. Wet–dry cycles affect dissolved organic carbon in two California agricultural soils. Soil Biol. Biochem. 31, 1031–1038. https://doi.org/10.1016/S0038-0717(99)00017-6.

Saha, D., Kukal, S.S., 2015. Soil structural stability and water retention characteristics under different land uses of degraded lower himalayas of north-west India. Land Degrad. Dev. 26, 263–271. https://doi.org/10.1002/ldr.2204.

Schumacher, B. a, 2002. Methods for the Determination of Total Organic Carbon in Soils and Sediments. Carbon N, Y.

Shelton, D.R., Parkin, T.B., 1991. Effect of moisture on sorption and biodegradation of carbofuran in soil. J. Agric. Food Chem. 39, 2063–2068. https://doi.org/10.1021/jf00011a036.

Sigua, G.C., Isensee, A.R., Sadeghi, A.M., 1993. Influence of rainfall intensity and crop residue on leaching of atrazine through intact No-till soil cores. Soil Sci. 156, 225–232. https://doi.org/10.1097/00010694-199310000-00002.

Six, J., Elliott, E., Paustian, K., 2000. Soil macroaggregate turnover and microaggregate formation: a mechanism for C sequestration under no-tillage agriculture. Soil Biol. Biochem. 32, 2099–2103. https://doi.org/10.1016/S0038-0717(00)00179-6.

Sposito, G., 2008. The Chemistry of Soils. Oxford university press.

Stehle, S., Schulz, R., 2015. Agricultural insecticides threaten surface waters at the global scale. Proc. Natl. Acad. Sci. Unit. States Am. 112, 5750–5755. https://doi.org/10.1073/pnas.1500232112.

Tisdall, J.M., Oades, J.M., 1982. Organic matter and water-stable aggregates in soils. J. Soil Sci. 33, 141–163. https://doi.org/10.1111/j.1365-2389.1982.tb01755.x.

Utomo, W.H., Dexter, A.R., 1982. Changes in soil aggregate water stability induced by wetting and drying cycles in non-saturated soil. J. Soil Sci. 33, 623–637. https://doi.org/10.1111/j.1365-2389.1982.tb01794.x.

Van Der Werf, H.M.G., 1996. Assessing the impact of pesticides on the environment. Agric. Ecosyst. Environ. 60, 81–96. https://doi.org/10.1016/S0167-8809(96)01096-1.