1 **The application of X-ray micro Computed Tomography imaging for tracing**

2 **particle movement in soil**

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26 **Abstract**

27 Despite significant advances in recent years in the application of sensing and imaging

28 technologies to the study of the hydraulic behaviour of soils, our understanding of how

29 solutes and particulate matter move through soil is still limited and often based on idealised

30 soil structures. The aim of this work was to use an appropriate proxy material, in this case

31 (Decabromodiphenyl ether (DBDE)), to represent 1-2 µm sized chemical particles, frequently

32 used in agricultural practices, in order to trace their spatial and temporal movement through a

33 soil column. X-ray Computed Tomography (CT) was employed to map the 3D pore geometry

34 and facilitate visualization of the concentration distribution of the highly X-ray attenuating

35 proxy material as it was applied and subsequently leached through the soil over a 5 hour

36 period. Simultaneously the soil eluate was collected from the bottom of each column and the

37 concentration of proxy material measured using Gas Chromatography to compare with the

38 imaged data. The method developed for visualising the tracer material in 3D at the pore-scale

39 was successful. The results demonstrated that the tracer material initially moved rapidly

40 through the upper portion of the soil but subsequently became immobile, despite repeated

41 elution with water as confirmed by imagery. Similar concentrations to those applied to the

42 soil surface were not recorded at any point in time towards the bottom of the soil column. By

43 visualising the DBDE distribution in 3D it was possible to correlate the highest

44 concentrations of the tracer material with the location of the smaller size pores (i.e.

45 mesopores). Dynamic X-ray CT imaging of tracer materials has considerable potential as a

46 proxy for the visualization of particulate agricultural chemicals that will assist with

47 understanding how their transport behaviour varies both spatially and temporally.

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51

52 **Introduction**

53 The UK National Action Plan for Sustainable Use of Pesticides (Defra 2013) encourages the

54 sustainable use of pesticides and highlights the importance of the life cycle of chemicals. As

55 intensification of agriculture accelerates to meet increasing food demand, it is becoming

56 increasingly important to understand precisely how agricultural chemicals interact with, and

57 move through, soil (Carvalho 2006). Such agrochemicals are known to cause contamination

58 in surrounding ecosystems when applied excessively (Gamon et al. 2003), therefore

59 development of sustainable management practices are essential to achieve both increased

60 crop production and decreased pollution. Improved understanding of agrochemical behaviour

61 in soil will contribute not only to the alleviation of environmental impact but also to the

62 possibility for improvement in controlled placement leading to increased bioefficacy and

63 reduced use rates.

64

65 The movement of agrochemicals through soil is strongly influenced by the physical, chemical

66 and biological characteristics of the soil and plants, as well as those of the chemical itself.

67 This intricate combination of influences makes understanding how an agrochemical moves

68 through soil both spatially and temporally extremely difficult. Traditional methods for

69 examining solute flow through soil have focused on conventional bulk *ex-situ* chemical

70 analysis of soil and eluate (Andreu and Picó 2004). Continuous soil column tests have been

71 routinely used to produce breakthrough curves to characterise the behaviour of the chemical

72 of interest (Brusseau et al. 1991). Such techniques have also been combined with

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73 mathematical models to predict chemical movement e.g. Magga et al. (2012). In combination

74 these approaches have been used to provide detailed information on the fate of chemicals

75 applied to soil, however research in this area has been hindered by a lack of real time data,

76 particularly from a three dimensional (3D) perspective. One technique that has shown

77 promise in this regard is X-ray Computed Tomography (CT) which allows the visualization

78 of the internal fabric of a porous media such as soil. With CT it is possible to non-

79 destructively visualize the internal pore geometry of the structured media and, with repeating

80 scanning, characterisation of the active processes *in situ* can be attempted assuming the

81 solute/particulate material can be distinguished from the soil background. X-ray attenuation is

82 linked to the material elemental composition; hence elements with a high atomic number

83 have a higher X-ray attenuation and are potentially good candidates to act as a tracer of solute

84 flow in a soil.

85

86 The use of tracers in X-ray CT imaging is routine in medical research to improve the contrast

87 of blood vessels and tumours and a wide range of tracers have been applied such as gold

88 nanoparticles (Nune et al. 2009) and iodinated agents (Lusic and Grinstaff 2012). There has

89 been limited research into the use of tracers to visualise solute movement in soil (Anderson et

90 al. 1992, Clausnitzer and Hopmans 2000, Anderson et al. 2003, Luo and Lin 2008). A key

91 limitation is that X-ray CT is best suited to the visualisation of motionless objects (Luo and

92 Lin 2008) as the scan process generates spatial data of the entire sample over the whole

93 course of the scan, with any effect of change in the material morphology typically corrected

94 at the end of the scan. However with the repeated scanning of the same sample over the

95 shorter timescales that is now achievable (as low as 5 minutes), it is possible to include time

96 as a variable providing the solute transport is not too rapid. Mooney (2002) used X-ray CT to

97 visualize soil water movement, identifying preferential flow paths, in soil columns by spatial

98 subtraction of images pre- and post-wetting. Anderson et al. (2003) combined X-ray CT

99 imaging with an iodide breakthrough experiment, and was able to compare the results with

100 laboratory derived measurements of saturated hydraulic conductivity. Luo and Lin (2008)

101 passed an iodide tracer through a soil column (30 cm) over a 23 hr period and repeatedly

102 scanned the soil column to demonstrate the spatial variation in hydraulic behaviour of the

103 soil.

104

105 To date there has been limited research concerned with tracking the movement of particles or

106 suspensions in soil using X-ray CT at the pore (µm-mm) and column (mm-cm) scales. In this

107 work we tested a novel proxy for agrochemical suspension concentrates, Decabromodiphenyl

108 ether (DBDE), chosen due to its X-ray attenuation properties and similar suspension

109 behaviour compared to routinely used compounds such as Chlorothalonil, a broad spectrum

110 fungicide which has an average particle size of 2 µm (Curry et al. 1998). The objectives of

111 this investigation were to determine the efficacy of DBDE as a general proxy tracer for

112 particulate agrochemical movement in soil via CT imagery and to investigate if X-ray

113 attenuation can be used as a surrogate for tracer concentration over time and following

114 elution by water.

115

116 **Materials and Methods**

117 *Soil column preparation*

118 Soil was obtained from the '18 acre' field site at Syngenta Jealott's Hill International

119 Research Centre, Bracknell, UK. The soil was a Brown earth with a sandy clay loam with 49

120 % sand, 27 % silt, and 24 % clay. Soil was sieved to < 2 mm and wetted to 17 % moisture

121   content; centrifuge tube filters were used as soil columns (23 mm diameter, 40 mm length),

122   with holes at the bottom to allow free drainage of soil solution. The outer tube holder was

123   used to hold the columns during scanning and to collect soil eluate. Six tubes, each

124   containing different concentration of the tracer suspensions used for calibration during the

125   image analysis process, were secured to the inside edge of each column, before the soil was

126   packed into the columns at a bulk density of 1g cm^{-3}. To examine tracer movement through

127   40 mm of soil, triplicate columns were packed to heights of both 10 and 40 mm and the

128   bottom 10 mm of each of these columns scanned to represent tracer movement at the top and

129   bottom of a 40 mm soil section, hence six columns in total. Eluate was collected from the

130   bottom of each section after each scan in a small container added to the bottom of the sample

131   for this purpose; the columns were left to saturate overnight the day before scanning.

132

133   *Tracer material and calibration*

134   DBDE (from Sigma-Aldrich) was chosen as the tracer material due to its high X-ray

135   attenuation capacity arising from the high electron density of bromine. It was milled using

136   Yttria Stabilized Zirconia Beads (0.3 mm) to generate particles with a size range of 0.1-6 µm

137   in diameter and a volume mean diameter (VMD) of 2-3 µm suspended in DI water with 5 %

138   Soprophor® 3D33 (tristyrylphenol polyethoxyester phosphate ester, Solvay) as a dispersing

139   agent. An initial test was undertaken to confirm that DBDE was detectable in soil and then to

140   identify the appropriate concentration for application (cross-sectional X-ray images of the

141   tracer and tracer embedded in soil are shown in Supplementary Figure 1). From this a DBDE

142   suspension was prepared with a concentration of 200 mg ml^{-1} and sonicated for 1 hour before

143   use. DBDE particle suspensions were then prepared with concentrations of 25, 50, 100 and

144   200 mg ml^{-1} and Kelzan S® (CP Kelco), a natural xanthan gum based thickener, was added

145 to reduce settling of particles over time. The suspensions were pumped into rubber tubing

146 (0.89 mm diameter) using a peristaltic pump after which the tubing was cut to 40 mm length

147 and sealed with PVA glue, before being secured to the side of each column with adhesive

148 tape.

149

150 *X-ray CT scanning procedures*

151 Each column was scanned using a Phoenix Nanotom® X-ray μCT scanner (GE Measurement

152 & Control Solutions, Wunstorf, Germany). Discrete regions of interest (ROI) only were

153 scanned at settings of 120 kV and 90 μA with a 0.1 mm copper filter. Projections (n = 1200)

154 were captured over a 30 minute time period for each column, with a pixel resolution of 12.5

155 μm, as such we do not resolve individual particulate material below this. Each column was

156 positioned so that only the base of the column (10 mm) was scanned i.e. the region 0-10mm

157 was scanned for half the treatments and the region 30-40mm for the other half. This

158 approach allowed us to directly relate the associated physical and chemical measurements of

159 these regions to the obtained X-ray images. Each of the six columns was scanned before, and

160 after, the application of 1 ml of DBDE (200 mg ml^{-1}) and then scanned a further 10 times

161 continuously over a 5 hr period. At the beginning of each post-DBDE scan 1 ml of water was

162 added to the top of the column and the soil eluate collected from the tube holder at the end of

163 each scan. A total of 72 CT scans were undertaken.

164

165 *Chemical analysis of DBDE*

166 Gas chromatography was used to determine the DBDE concentration in the eluate collected

167 from the bottom of each soil column after each scan (i.e. 30 min intervals). The aqueous soil

168 eluate samples containing DBDE particles were dried using a Genevac HT-4X centrifugal

169   vacuum evaporator. Toluene was added to the dried deposit to dissolve the DBDE after

170   which the samples were centrifuged to remove soil particles. Samples were diluted further in

171   toluene as required before analysis by gas chromatography using an Agilent 6890 Series GC

172   System, equipped with cool on column injection system, a fused silica DB-5 column (15 m x

173   0.25 mm id; 0.25 µm film thickness) (Agilent J&W, Agilent Technologies) and an electron

174   capture detector. The peak area for DBDE was used to calculate the DBDE concentration of

175   the sample, with reference to a calibration standard. By determining the concentration of

176   DBDE collected from the eluate of each section it was possible to construct a chemical

177   breakthrough curve for each section of the soil column by plotting % recovery over time.

178

179   *Image processing and analysis*

180   The radiographs of each scan were reconstructed in 32 bit format to avoid compression of the

181   greyscale histogram, which is especially important when attempting segmentation of

182   materials with similar attenuation. After reconstruction each image volume of 10 mm x 23

183   mm diameter was imported into Volume Graphics (VG) StudioMAX® 2.0 and the images

184   cropped to a cylindrical shape with a height of 7.76 mm and diameter of 2.3 mm. A median

185   filter of 3 pixels was applied to correct for any residual noise.

186

187   *Suspension concentration calculations*

188   A region within each tracer calibration tube was manually selected and the average greyscale

189   value within it was calculated using the volume analyser tool in VG StudioMAX® 2.0. The

190   average greyscale values along with the known DBDE concentrations were used to calibrate

191   each scan to calculate the concentration of the tracer. It was important to undertake this

192   process for each individual scan even though time consuming as brightness (and hence

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193 greyscale value) can vary between CT scans due to ageing of the X-ray tube filament thus

194 influencing the image segmenting process.

195

196 *Segmentation of pore space*

197 The calibration tool in VG StudioMAX® 2.0 facilitates a thresholding technique that can be

198 used to create ROIs based on pre-selected greyscale values chosen to represent the

199 background and the material. We observed three clear ROIs for soil, solute-filled pores and

200 pores filled with only highly attenuating tracer particles (seen as the white particles in Figure

201 1B-D). The distinction between solute filled pores and tracer filled pores was the former,

202 which we attribute to the added solution that contains DBDE and tracer filled pores, had a

203 significantly lower X-ray attenuation than the latter which we attribute to aggregated, settled-

204 out DBDE particulate material. This was confirmed in the elution studies were the location of

205 solute filled pores varied over time and the tracer filled pores did not. It was not necessary by

206 this approach to segment the air-filled pores though this would have been straightforward if

207 necessary. Figure 1 illustrates the method used for creating ROIs for the total tracer filled

208 pores (C), essentially the combination of ROIs for solute filled pores (A) and deposited tracer

209 filled pores (B). The volume analyser tool was used to provide the average greyscale value

210 and the volume of each ROI, as well as an individual greyscale histogram. The average

211 greyscale value of the final ROI was then used to derive the relative tracer concentration of

212 the tracer in each scan. To ensure that no residual soil mineral material was included in the

213 calculation of the deposited tracer filled pores, soil mineral content was segmented using the

214 automatic threshold option in VG StudioMax and then the histogram frequency data of the

215 solute filled pores and the mineral portions were aligned and the frequencies subtracted. The

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216 average greyscale value was then recalculated using the new frequency list and the resulting

217 concentration determined.

218

219 *Pore size analysis*

220 In order to examine the relationship between soil pore size and tracer concentration, the

221 images of the tracer filled pores only i.e. settled out DBDE as described above were imported

222 into the image processing software ImageJ 1.46r. Here it was possible to separate the pores

223 that were filled with highly attenuating deposited tracer material into two classes based on

224 size, in this case pore diameter. We used the size classes as described by Brewer (1988);

225 meso-pores $30 - 75$ µm and macro-pores > 75 µm to separate the pores within each image.

226 Image stacks of these pore sizes were imported back into VG StudioMAX® 2.0 to obtain the

227 average greyscale value data and hence concentration of DBDE.

228

229 **Results**

230 Figure 2A shows a typical greyscale X-Y image of soil produced from an X-ray CT scan. The

231 composition of the soil material is displayed in a range of grey shades that are visible due to

232 differing levels of X-ray attenuation. The average greyscale values were determined via the

233 calibration tubes that were placed on the outside of the soil column during the scanning

234 process to represent concentrations of 25, 50, 100 and 200 mg ml^{-1} respectively

235 (Supplementary Figure 1). There was a strong relationship between DBDE concentration and

236 X-ray attenuation ($R^2 = 0.98$), which can be seen by eye, as concentration increases the

237 material within each tube appears lighter in colour. Figure 2B shows a scan taken from the

238 same location as Figure 2A, after the addition of 1 ml of the DBDE tracer (200 mg ml^{-1}) with

239 the highly attenuating tracer visible in the soil pores. The final binarised image (Figure 2C)

240   highlights just the tracer filled pores (in white) after removal of the surrounding soil and

241   mineral grains. Using the average greyscale value of the tracer-filled pores from each image,

242   a value for DBDE concentration could be derived from the calibration graph.

243

244   By repeated washing through of the DBDE with water, and subsequent re-scanning, a tracer

245   breakthrough curve (Figure 3) was obtained for each of the 10 mm soil sections. The mean

246   concentration of tracer in the uppermost 10 mm section immediately following application of

247   DBDE was 80 mg ml^{-1} which declined rapidly over a 3 hour period to 42 mg ml^{-1}. The

248   concentration continued to decline over the next 2 hours, albeit at a slower rate, and reached

249   28 mg ml^{-1} at the end of the experiment. This incomplete breakthrough is supported by the

250   low concentration of tracer in the lowermost 10 mm section (30-40 mm depth in Figure 3)

251   where the concentration showed a slight increase over time but no defined peak

252   breakthrough.

253

254   The same trends were observed in the Gas Chromatography recovery of DBDE (Figure 4).

255   The eluate collected from the bottom of the 0-10 mm section had an initial peak recovery of

256   15.7% of the total added DBDE, which rapidly declined after the first 1 hour 30 minutes to

257   4.5%, before decreasing to <1% by the end of the 5 hour period. The recovery from the 30-

258   40 mm section was different; after the addition of the DBDE the recovery was <1% which

259   increased to 3.6 % by 90 minutes declining to 2.6% by the end of the experiment. After 3

260   hours the recovery from the eluate collected from both sections was broadly similar.

261

262   To understand more about the effect of pore size on tracer transport, the tracer filled pores

263   category were separated into two groups defined by diameter, meso-pores, 30 µm-75 µm and

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264 macro-pores, >75 µm. Figure 5A demonstrates how the distribution of the tracer changed

265 over time in the uppermost 10 mm section of the soil column. Initially the soil was very wet,

266 with only 16 % of the pores of the total pore volume air filled (as derived by imagery hence

267 limited to the resolution used in this study). As the tracer infiltrated the soil, the proportion of

268 air-filled pores increased due to drainage despite the repeated washing through of water, and

269 the proportion of tracer-filled pores decreased in both the macro-pores and meso-pores

270 classes. The volume in the macro-pores remained higher than that of the meso-pores

271 throughout (mesopore volume was <15% of the total pore volume by the imaging approach

272 and classification used here). Figure 5B illustrates the link between pore size and

273 concentration, only for the tracer-filled pore category, showing that while the concentration

274 of the tracer in both the meso- and macro-pores decreased, it remained consistently higher in

275 the meso-pores despite this only accounting for a small part of the total pore volume. The

276 relationship between the concentration of solute and tracer filled pores (derived by the

277 calibration from the X-ray images) and pore size is visualised in 3D over time in Figure 6.

278 Tracer movement is revealed to be less rapid than the associated redistribution of water

279 through the repeated washing through process; in addition, the higher concentration of DBDE

280 in the smaller sized pores is clearly visible.

281

282 **Discussion**

283 DBDE in suspension has been shown to be a useful particulate tracer material from an

284 attenuation perspective, which highlights its potential to act as a proxy for active ingredients

285 used in agrochemicals. The use of calibration standards for each sample/scan enabled an

286 accurate construction of the DBDE tracer breakthrough helping to remove the influence of

287 any fluctuations caused by X-ray CT parameters (Clausnitzer and Hopmans 2000). However

288　we identified issues with its mobility beyond a shallow layer of soil. The breakthrough results

289　clearly demonstrated low particle breakthrough in the soil column at 40 mm depth (Figure 3).

290　This lack of movement occurred despite the addition of water every 30 minutes.　This

291　contrasts with the results in the upper 10 mm where significant movement occurred in the

292　early part of the experiment before rapidly declining suggesting that particles of DBDE were

293　immobilised within the soil column. These data were confirmed by the recovery analysis in

294　the eluate. Similar studies have also observed this for non-soluble particulate agricultural

295　chemicals i.e. following application there is initial, limited movement but when leaching

296　stops (Noling 2012) further movement only occurs if particles are dispersed (Paradelo et al.

297　2013). This is highly relevant to the development of new particulate morphological

298　arrangements for agrochemicals that might have better mobility than the DBDE used here,

299　though noting that there are advantages, such as increased residency, associated with the

300　reduced mobility of compounds such as pesticides in soils. The extent to which mobility

301　could be enhanced via a reduced particulate size or use of surfactants would be worth further

302　research. As would the assessment of whether mobility of the tracer could be improved

303　beyond the time period of elution in this study..

304

305　The pore morphometric data suggests the majority of the pores were filled following the

306　tracer application and as water was applied, the volume of tracer filled pores decreased over

307　the first 3 h of the experiment. After this stage the tracer particles were likely to have settled

308　out of suspension illustrated by the lack of concentration change in each section after 2.5 h.

309　Figure 5 shows that the concentration of the tracer in the meso-pores was continually higher

310　than in the macro-pores, indicating that the particles collected in smaller pores and did not re-

311　suspend easily, preventing complete breakthrough. Paradelo et al. (2013) made similar

312 observations when examining the transport of Cu bound to soil particles, using particle

313 breakthrough curves combined with X-ray CT, indicating if particles did re-suspend, they

314 might only move short distances and then reclog pores. Meso-pores occupy a size range

315 within soil referred to as the 'storage pore' size range; 0.5-50 µm. These are often pores

316 located within soil aggregates where water is held strongly and drainage is unlikely (Cornejo

317 et al. 2004). One possibility for future studies is to consider that the combination of particle

318 size and soil pore size used here was sub-optimal for enhanced particulate transport and that

319 soil larger pores and/or smaller particles might have been more mobile.

320

321 The linking of soil pore characteristics to tracer movement highlights new capabilities for the

322 use of X-ray CT in soil hydrology studies. Clausnitzer and Hopmans (2000) stressed the

323 need for higher resolution in order to improve the accuracy of breakthrough experiments.

324 Here we obtained a resolution of 12.5 µm, significantly higher than most comparable studies

325 e.g. 86 µm (Clausnitzer and Hopmans 2000), 105µm (Luo and Lin 2008) and 2mm

326 (Anderson et al. 2003). The benefits of higher resolution and repetitive scanning is the

327 temporal pore-scale view (Figure 6), illustrating the difference in concentration between the

328 tracer filled pores, in addition to the movement of DBDE. Despite the improvement in

329 resolution, visualization of individual tracer particles was not possible here however via

330 synchrotron imagery this would be possible albeit on smaller samples than considered here.

331 Using our approach the overall particle movement can be derived from the movement of the

332 suspension. The majority of the previous research that account for water flow mechanisms in

333 soil have considered solute tracers rather than particulate material. However there has been

334 widening research into particle movement in soil, in particular relating to chemical fate where

335 natural occurring particles can either enable or prohibit the transport of adsorbed chemical

336 species (Kretzschmar et al. 1999, de Jonge et al. 2004, Sen et al. 2004) which highlights the

337 importance of this area for further study.

338

339 **Conclusions**

340 X-ray CT offers a previously unachievable method for non-destructive 3-D visualization of

341 tracer material embedded within soil through time. The method developed here not only

342 illustrates movement of tracer in the soil but also the concentration. The behaviour of the

343 tracer can then also be directly linked to the soil pore architecture. In this research we have

344 demonstrated that the tracer, DBDE, was mobile only for a short time period (up to 3 hrs)

345 after which it became immobile despite repeated elution of the soil column. From an agro-

346 chemical perspective this would have advantages and disadvantages. By imaging the pore

347 structure it was possible to show that the pore size in particular has a significant influence on

348 the retention and concentration of the tracer. Whilst definitive conclusions regarding specific

349 agricultural chemical particulate behaviour cannot be drawn from this experiment alone,

350 DBDE quantified by X-ray CT has shown potential as a proxy for the visualization of

351 particulate agricultural chemicals to help assist management decisions concerned with their

352 fate in the rootzone and wider environment though further work is required across a range of

353 particulate sizes and soil pore size/type combinations. Such studies could also be used to

354 direct future research into optimising the morphological design of the particulate material

355 used in future agrochemicals.

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