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Lucherini, Andrea; Gonzalez-Ollauri, Alejandro; Mickovski, Slobodan B.

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The effect of vegetation on soil polluted with galligu: phytostabilisation and novel approaches to evaluate soil galligu concentration

Andrea Lucherini[1], Alejandro Gonzalez-Ollauri[1,2,3], Slobodan B. Mickovski[1, 2]

[1]*School of Computing, Engineering and Built Environment, Glasgow Caledonian University, G4 0BA Glasgow, UK*

[2]*The BEAM Research Centre, Glasgow Caledonian University, G4 0BA Glasgow, UK*

[3] *Corresponding author: alejandro.ollauri@gcu.ac.uk*

Abstract

The Sightill area, situated north of river Clyde in Glasgow, is polluted with the waste product galligu as a consequence of past activities associated with the alkali industry. As this area is planned for re-development, it is necessary to explore feasible ways of polluted soil decontamination. An experimental laboratory survey was conducted to assess whether phytostabilisation could be a suitable strategy to limit the mobilisation of galligu within contaminated soil. For this purpose, two different types of vegetation were tested - i.e. a male dwarf fern (*Dryopteris Affinis* (Lowe) Fraser-Jenk) and alfalfa (*Medicago Sativa* L.). Laboratory experiments were conducted using readily available materials to study both the axial and vertical movement of galligu in the soil as a result of heavy rainfall events. In addition to this research, original and simple methods were tested to assess whether it was possible to estimate galligu content within a soil volume. The results showed that sediment loss was reduced by 84% and 94% under fern and alfalfa covers, respectively, compared to fallow soil. The concentration of galligu in the sediments from fern and grass treated soil was 59% and 62% lower, respectively, than under fallow soil conditions. Furthermore, alfalfa was observed to be more effective in containing galligu, since the fern root systems may have allowed the contaminant to percolate towards the bottom of the soil. Turbidity and colour-based analyses were able to give an estimation of the concentration of galligu in the soil effectively. The results of this research are directly applicable to phytoremediation actions on polluted soils and to the assessment of synthetic soil pollutants using simple and inexpensive methods.

Keywords

Geoenvironment; Land contamination; Pollution

1. Introduction

Galligu is an industrial, toxic, solid waste mainly comprising calcium sulphide (CaS), and often found in soils polluted by heavy metals and other hazardous elements. Galligu is generated by the Leblanc process, which is employed to produce soda ash (i.e. sodium carbonate) (Aftalion,1991). The Leblanc process is based on two separated stages: (i) production of sodium sulphate (Na_2SO_4) or "salt cake" through the (NaCl) and sulphuric acid (H_2SO_4) – i.e. $2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HC$; and (ii) production of CaS and sodium carbonate (Na_2CO_3) through the reaction between the resulting Na_2SO_4 from Step 1 and calcium carbonate ($CaCO_3$) -i.e. $Na_2SO_4 + 2C + CaCO_3 \rightarrow Na_2CO_3 + CaS$. The Leblanc process was widely used in soda production plants throughout the 19th Century in France and Great Britain, with Great Britain once producing over 200,000 tons of soda per year. For each ton of Na_2CO_3 generated, 2 tons of galligu were produced (for review see Aftalion, 1991). Since galligu had no economic value, it was dumped and spread on open fields near the processing factories. Although galligu production and tipping do not exist anymore (the Leblanc process was replaced by the Solvay process in the late 19th Century; Kiefer, 2002), the galligu remaining at brownfield sites still poses a serious environmental threat, jeopardising the quality of soil and water.

To date, the most common treatment method used to control galligu pollution in *situ* is stabilisation/solidification using cement – i.e. encapsulation (Halton Borough Council, 2013). The encapsulation of contaminants through solidification is widely used for controlling soil heavy metals (Bocanegra, et al., 2017; Li & Poon, 2017), pesticides (Shukla, et al., 1992) and organic waste (Vipulanandan & Krishnan, 1990), too. An alternative, chemically-based technique to encapsulation is known as ACT (Accelerate Carbon Technology), in which cement is mixed with gaseous carbon dioxide to seal the polluted soil under treatment (Bertos, 2004). However, the two techniques mentioned above are not environmentally friendly, as they are based on the injection of synthetic materials into the environment and the release of contaminants back into the environment is possible after encapsulation (Moore et. Al, 2003). Alternative green techniques or nature-based solutions, such as phytoremediation, have not been explored before for the reclamation of land polluted with galligu.

Phytoremediation comprises the use of vegetation and associated microbes to reduce the concentration and toxic effects of pollutants in contaminated environments (Greipsson, 2011). It is a cost effective eco-friendly, and socially accepted approach that has been used to tackle soil and water pollution problems over the last 300 years (e.g. McCutcheon and Rock, 2001). Phytoremediation has been implemented successfully in the clean-up of soils polluted with heavy metals (Muthusaravanan, 2018), or in the removal of nitrogen from the water using treatment wetlands (Kinidi & Saleh,2017). The cost of phytoremediation of one cubic meter of soil can be between 1000 and 100000 times lower than conventional soil remediation (Ghosh, 2005). Multiple physiological processes undertaken by different plant species can be considered for reducing the concentration of pollutants in the environment or promote their immobilisation – e.g. phytoextraction, phytostabilisation, phytovolatilisation, phytotransformation, and phytofiltration (for review see Rahman, 2011). The specific phytoremediation process will depend on the soil pollutant and on the chosen plant species – i.e. not all species are able to withstand, uptake, or accumulate any or specific pollutants (Malayeri, 2008). In the case of galligu, phytostabilisation could be a potential viable alternative to conventional remediation methods like encapsulation.

Sites polluted with galligu are usually co-contaminated by other toxic materials, such as heavy metals (Gomes, 2016). This issue should be taken into account upon selecting plant species – a key step to succeed with a given phytoremediation action. Some members of the *Dryopteridaceae* fern family are able to tolerate and accumulate heavy metals (i.e. hyperaccumualtors) and their phytoremediation potential has been tested before (e.g. Raquel, 2012; Ruiz-Chancho, 2008; Tremlovà, 2016). However, *Dryopteris affinis* (Lowe Fraser-Jenk), a dwarf fern native to Scotland, has never been tested for phytoremediation purposes. This is an important aspect for future applications, as the use of native species for remediation actions should be more ecologically sound (Pimentel, 2005). Alternatively, other fast-growing species may be considered for phytoremediation purposes (Wang, et al., 2008), e.g. alfalfa (*Medicago Sativa* L.) - a leguminous, perennial, cosmopolite, and fast-growing herb (Bonfranceschi, et al., 2009). Alfalfa has shown stabilising potential on acidic copper mine tailings (Chen, et al., 2015) as well as on pyrene (Wang, et al., 2012), stabilising heavy metals and hydrocarbons (Agnello, et al., 2016). In addition, alfalfa has a fibrous root system able to trap contaminants effectively, reduce erosion, and stabilise soil materials (Hao, et al., 2004; Gonzalez-Ollauri and Mickovski, 2017a).

The aim of this paper is to investigate whether phytostabilisation can be considered a viable solution to immobilize or limit the movement of galligu in polluted soil. By using male dwarf ferns and alfalfa under laboratory conditions, the observations will focus on the ability of vegetation to reduce the axial and vertical transport of galligu after simulating heavy rainfall events. To complement the assessment of the effectiveness of phytostabilisation against galligu-polluted soil, this paper also strives to explore potential, simple, cost-effective, novel approaches for quantifying the concentration of galligu in polluted soil and runoff under resource-limited situations. For this objective, the viability of two different analytical approaches will be elaborated: (i) turbidity; and (ii) image analysis.

2. Materials and methods

2.1. Soil and galligu characterisation

Galligu samples were retrieved from Sighthill, Glasgow, Scotland (Longitude: -4.231040, Latitude: 55.871420) together with a bulk sample of uncontaminated soil. A mass of 1.5 kg of galligu was collected with a shovel from each one of 20 different sampling points separated 2 m apart from each other. A mass of 20 kg of soil not contaminated with galligu was also excavated form the same site. The retrieved samples were placed in sealable PVC bags and stored in a cold, dry, and well-ventilated room to prevent any potential spreading of fumes. Particle size distribution and specific gravity tests (BSI, 2013) were undertaken for both galligu and soil materials. In addition, pH measurements using the slurry method (ASTM, 1995) were conducted on both pure galligu and soil-galligu mixtures using a pH electrode (Fisher Scientific ACCUMET BASIC AB15; previously calibrated at pH 4.0 and 9.0) in order to scope more information about the physicochemical properties of the samples.

2.2. Substrate preparation

Galligu and soil materials were dried in an air-assisted oven at 80°C for 24 hours until constant mass was achieved. The materials were then broken manually – first with a hammer and then with pestle and mortar. Soil and galligu were sieved separately through a 2 mm diameter sieve (BS ISO 11277:2009; ISO/TC 190, 2009). Then, a 50:50 mass mixture of galligu and uncontaminated soil was prepared from the dried and sieved samples and was used as substrate for plant growth.

2.3 Axial transport of galligu

2.3.1 Axial soil column preparation

Six axial soil columns were prepared at the Hydraulics Laboratory, Glasgow Caledonian University to test the axial transport of galligu following runoff simulation tests. The axial soil columns were prepared using PVC pipes with dimensions of 500mm x 100mm x 50 mm, cut in half, and tilted 20 degrees from the horizontal to foster runoff (Fig. 1). Each half pipe was filled with plant growth substrate with a bulk density of 1.26 g cm^{-3} up to 2/3 of its length. The remaining third was used as a buffer zone and was filled with uncontaminated soil (Fig. 1) in order to evaluate the potential movement of galligu following the runoff simulations. Ferns and alfalfa were grown only on the soil-galligu mix substrate, and no vegetation was established within the buffer zone (Figure 1). Two replicates of three different ground covers (6 test beds in total) were established on the columns – i.e. fern, alfalfa, and fallow soil. At the column ends, small openings were cut to allow the flow of water and solids. Additionally, small plastic trays were placed at the column ends to collect water and sediment transported with the runoff (Fig. 1).

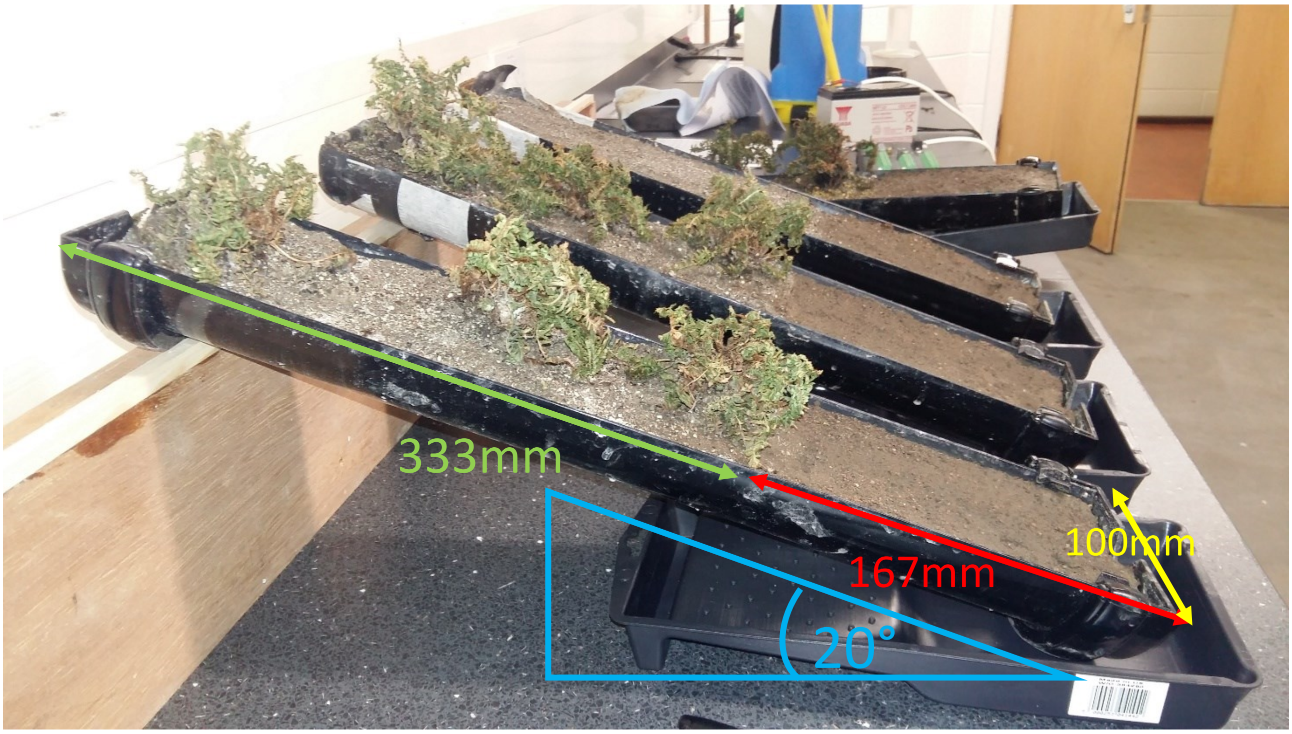

Figure 1. Axial soil columns used for runoff simulations. The contaminated area is labelled in green, while the buffer zone in red. See online version for colours.

To establish a vegetated ground cover with ferns on the model soil columns, twenty-five individuals of *Dryopteris affinis* (Lowe Fraser-Jenk) were sourced from Shady Plants Fern Nursery (Clashmore, Rep. Ireland). The fern individuals were stored in the laboratory for a period of seven days to enable adaption to the new environmental conditions. During this period, the fern individuals were stored at 24°C under a 36 W BIOLUX© fluorescent lamp placed 300 mm above the ferns. The plants were watered every two days with 25 mL of tap water. After this period, the plants were carefully removed from their pots and the root systems were cleaned carefully from the remaining soil using a water jet. After air drying each root system, the plants were transplanted into the prepared substrate (Section 2.2) after adding a small amount of compost into planting holes to provide a dose of nutrients and lower the transplantation shock (Espiritu, 2016). Three planting holes were created in each axial column (a total of 6 ferns; Figure 2), spaced 50 mm from the column edges and between individuals. Once the fern ground covers were established on each axial soil column, these were placed under a fluorescent lamp for a week and the soil was covered with PVC membrane to retain moisture and promote mulching. Each column was watered daily with 100 mL of tap water.

Figure 2 Preparation and transplantation of ferns into an axial soil column.

To establish an herbaceous ground cover on the model soil columns, 10 g of alfalfa seeds were evenly spread on the surface of the columns, watered and placed under a fluorescent lamp. The seeded columns were kept under a black PVC membrane for 2 days to retain moisture and promote mulching until germination. After germination, the membrane was removed and the columns were placed under a fluorescent lamp for 4 weeks. After 1 week from germination, 20 mL of fertiliser solution (15mL of Miracle-Gro® Water Soluble All Purpose Plant Food fertilizer diluted in 4.5 L of water) were added manually every 5 days.

2.3.2 Runoff simulation tests

To generate runoff on the axial soil columns, rainfall was simulated by using a 20 L backpack sprayer. The nozzle was kept at 100 mm above the soil surface and moved manually to sprinkle water evenly over the portion of the axial soil column containing polluted soil (Fig. 1). Rainfall intensity was pre-monitored and maintained at a rate of 36 mm $hour^{-1}$, mimicking a heavy rainfall event (MET Office, 2007). This resulted in the application of 200 mL of water for 15.5 seconds for each simulation run. In total, 12 simulation runs were implemented (i.e. 6 events in one hour) over two days, separated by 24 hours without further water additions to allow the soil to dry. The first simulation run was undertaken when the soil in the axial columns was fully saturated with the aim of fostering runoff.

2.3.3 Solid Materials Transport

The solid materials transported with the runoff generated from the rainfall simulation events were collected in plastic trays placed at the end of the axial soil columns (Fig. 1). The total runoff volume was measured with a volumetric cylinder. Subsequently, the collected suspension – i.e. water plus soil solids – was placed in aluminium trays that were then placed in an oven at 80°C for 24 hours to eliminate the liquid portion and quantify the proportion of solids transported in the runoff. The sediment load resulting from each rainfall event was calculated by dividing the mass of solids carried in the runoff by the corresponding mass of water carried in the runoff. In addition, the hydraulic flux through the axial soil columns was estimated by dividing the volume of water collected after each rainfall simulation event by the duration of these events. With this, we strived to investigate whether the presence of vegetation could affect the amount of water infiltrating into the soil. Eventually, three core soil samples were collected with an apple corer from the buffer zone (Fig. 1) of each axial column (i.e. 18 samples in total). To do so, a random sampling approach was followed to collect soil cores from the top, middle, and bottom part of the buffer zone. The soil core samples were oven-dried at 80°C for 24 hours and stored until further analysis.

2.4 Vertical transport of Galligu

2.4.1 Vertical soil columns preparation

Eight vertical soil columns were built using transparent PVC cylinders of 200 mm height and 60 mm diameter. Each cylinder was filled with uncontaminated dry, sieved soil (Section 2.2) up to a 150mm height from the bottom. The remaining cylinder volume was filled with a 50:50 galligu-soil mixture (Section 2.2). At the bottom of each column, a nylon mesh with 0.2 mm apertures was installed to sustain the soil, and capped with perforated plastic lids to allow water flow through the column (Figure 3). We replicated the same treatments (i.e. ground covers) in the vertical columns as for the axial soil columns (Section 2.3) – i.e. 3 vegetated with ferns, 3 with alfalfa, and 2 under fallow cover as control. Ferns were prepared for transplantation following the same steps indicated in Section 2.3 and then inserted in the soil column with their root tips in contact with the uncontaminated soil horizon – i.e. 50 mm below the ground level (b.g.l). With this, we intended to encourage the fern roots to grow towards the bottom through the uncontaminated soil. For the columns with an herbaceous cover, 2 g of alfalfa seeds were evenly spread on the column surface. The surface of all eight prepared soil columns was covered with black PVC membrane to allow mulching and germination of the seeds, and to keep the roots moist. After germination, the columns were placed under a 60 W incandescent lamp placed 300 mm above the soil columns. The columns were water saturated from the bottom to prevent vertical deposition of galligu before simulating rainfall. A plastic cone was installed at the top of the columns to prevent water overflow during the simulation runs.

Figure 3 Vertical soil column preparation (diameter 60mm). (a-c) The nylon mesh is placed at the bottom of the column and covered with a plastic cap and fixed with dark tape (d) seeds spread on the top of the vertical soil column. The black mark shows the limit between pure and contaminated soil

2.4.2 Percolation tests and evaluation of the vertical transport of galligu

To assess the vertical transport of galligu in the soil, we conducted a series of percolation tests on fully saturated vertical soil columns by simulating a series of rainfall events. Each rainfall simulation run consisted in the application of 17 mL of water manually with a Pasteur pipette over 5 seconds, maintaining the same rainfall intensity of 36 mm $hour^{-1}$ as for the axial tests (Section 2.3.2). Rainfall simulations were carried out six times over a period of 12 days, leaving one day between simulation runs. The time necessary for the water to fully infiltrate in the soil columns after each rainfall simulation event was recorded with a stopwatch. During the simulations, the columns were placed on plastic trays to collect the drained leachate. The leachate volume was measured with a volumetric cylinder after full infiltration was observed. At the end of the series of rainfall simulations, the soil columns were extracted from the cylinders. Then, the vertical movement of galligu through the column was assessed visually. For this, we measured the displacement of the boundary between polluted and unpolluted soil with a ruler. Subsequently, three soil samples were taken from three different locations (i.e. top, middle, bottom) within the polluted soil column zone (i.e. top third). The soil samples were oven-dried at 80 C for 24 h and stored for further analysis.

2.5 Galligu concentration in the soil

2.5.1. Determination of Galligu concentration through turbidity analysis

We attempted to quantify the concentration of galligu in the soil by conducting a series of turbidity tests using a UV-VIS spectrophotometer (Thermo Scientific® GENESYS 105 UV-VIS). Firstly, we built a calibration curve as a reference for determining the concentration of galligu in suspensions with known galligu concentration. To do so, we made mixtures containing 2 g of soil and a varying concentration of galligu – i.e. 0 wt%,25 wt%, 50 wt%,75 wt%, and 100 wt%. The mixtures were introduced into 50 mL centrifuge test tubes and topped up with distilled water. Subsequently, the suspensions were shaken with a rotatory mechanical shaker for 10 minutes. Then, 5 mL of the turbid suspension were retrieved with a Pasteur pipette and analysed with a spectrophotometer at a wavelength of 400 nm (Orion Method AQ4500, AMI Turbiwell, EPA method 180.1). The absorbance of the suspensions was measured at 4 different time intervals (i.e. 2 min,10 min,15 min, and 20 min) to reduce the possible bias produced by the sedimentation of galligu particles over time. Once the calibration curve was built, the galligu concentration in the samples taken from both axial and vertical transport tests was quantified in relation to the benchmark concentrations established by the calibration process. To this end, suspensions were created with 2 g of sample and distilled water in 50 mL centrifuge tubes. Then, we followed the same steps described above for the calibration process. The concentration of galligu (wt%) in a sample was averaged between the concentrations measured at four different time intervals (i.e. 2 min, 10 min,15 min, and 20 min).

2.5.2 Determination of Galligu concentration through digital image analysis

We also attempted to determine the concentration of galligu in the soil through the analysis of digital images taken from galligu-soil mixtures and from the samples collected after the axial and vertical transport tests (see Sections 2.3.3 and 2.4.2). To this end, a calibration process was undertaken first, in which three concentrations of galligu were considered – i.e. 0 wt%, 50 wt%, 100 wt%. Galligu and soil mixture suspensions were made as described in Section 2.2. With regard to the samples collected after the axial and vertical tests, the solids were let to sediment completely and the liquid fraction was removed by drying under a 60 W incandescent lamp for 24h. The solid fraction was then spread into a thin, flat layer, ensuring that ridges or scars that could cast shadows on the digital images were not visible. The same steps were followed for the samples retrieved from the axial and vertical tests (Sections 2.3 and 2.4).

Digital photographs of the solid fraction layers were taken from a vertical distance of 500 mm using a 14 Megapixel Fujifilm® Finepix S3200 camera. To do so, the layers were illuminated under a 36 W BIOLUX® fluorescence lamp. Digital image analysis was undertaken using ImageJ v.1.51n software (Schneider, et al., 2012). To proceed with the image analysis, a colour frequency histogram was generated from the images to determine the pixel value belonging to soil and galligu particles, respectively. Through trial and error, it was observed that the optimal conditions for capturing digital images of soil-galligu mixture occurred when solid materials were slightly moist. These conditions increased the colour contrast between galligu and soil and, thus, made it easier to distinguish soil and galligu particles. Hence, dry mixtures of soil and galligu needed to be wetted prior to being photographed

Cumulative distribution functions (CDFs) were built from the image histograms and compared through Kolmogorov-Smirnov tests (Kolmogorov, 1933). The CDFs from each sample were compared against 3 benchmark CDFs from the samples with known galligu concentration described above. The latter step was used to determine the concentration of galligu in the samples retrieved after conducting the axial and vertical transport tests. The obtained results were then compared against the galligu concentrations obtained from the turbidity analyses to assess whether the two tests were in agreement with each other.

2.6 Statistical analysis

Statistical tests were carried out to evaluate statistically significant differences between the three ground covers - i.e. ferns, alfalfa, and fallow soil – established on the axial and vertical soil columns following rainfall simulations. Normality tests were undertaken first by inspecting visually the density function plot for each of the studied variables (i.e. sediment loss, runoff discharge, galligu content, percolation time). Statistically significant differences between the three ground covers were assessed through one-way ANOVA analysis (Marvin & Bishop, 1993) and with Kruskal-Wallis tests (Kruskal & Wallis, 1952) when data were and were not normally distributed, respectively. For axial soil transport, the analyses were conducted on 6 different samples (i.e 2 with ferns, 2 with alfalfa, 2 unvegetated), with 12 observations on the amount of solids loss each, for a total of 72 observations. The same number of samples were analysed for inspecting runoff discharge. For galligu content on axial runoff sediments, 5 observations were made on each sample, for a total of 30 observations. On vertical transportation tests, when measuring the percolation time, the number of observations were 36 per sample. For this test, 3 samples were prepared with ferns, 3 with alfalfa and 2 unvegetated, so the total amount of observations were 288. In vertical samples, galligu was sampled only in 3 different depths (i.e. 50mm, 100mm, 150mm; Fig. 13) so for this test, the number of observations was 24.

3. Results and Discussion

3.1. Galligu concentration in the soil

3.1.1. Determination of the galligu concentration in the soil through turbidity analysis

The regression line from the calibration process to determine the concentration of galligu in the soil through turbidity analysis is shown in Fig.4. The observed absorbance for the soil-galligu-water suspensions (Section 2.5.2) are shown in Table 1. Absorbance was higher in samples with no galligu, and it tended to drop over time due to particle sedimentation. From these results, we were able to build a regression line for each of the tested galligu concentrations (Fig. 4) to be used as benchmark for the determination of the concentration of galligu from the samples collected following the axial and vertical transport tests. In the light of our results, the turbidity test appears to be viable to estimate the concentration of galligu in the soil.

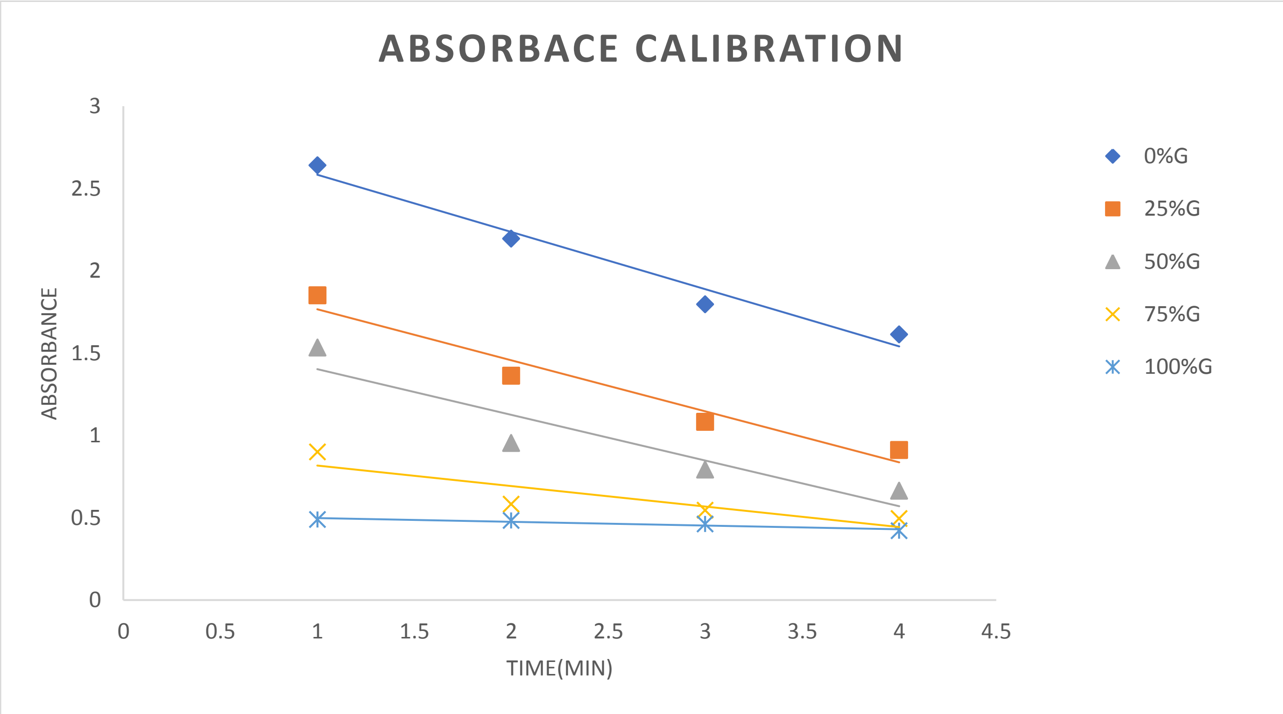

Figure 4. Regression line belonging to the calibration process through turbidity analysis (see Section 2.5.2a) for 5 different concentrations of galligu in the soil.

Table 1 Recorded absorbance over time for known concentrations of galligu in the soil determined through UV spectrophotometry.

Galligu concentration (%)	Sedimentation time (minutes)			
	2	10	15	20
0	2.641	2.197	1.798	1.6145
25	1.851	1.363	1.082	0.911
50	1.534	0.954	0.793	0.664
75	0.900	0.582	0.545	0.496
100	0.489	0.484	0.462	0.421

3.1.2 Determination of galligu concentration in the soil through digital image analysis

The concentration of galligu in the soil was estimated through digital image analysis by comparing the cumulative distribution functions (CDFs) retrieved from the different images' histograms (Fig.5) through Kolmogorov-Smirnov (K-S) tests (see Section 2.5.2.2). Accordingly, the K-S distance between the CDFs for each of the analysed soil samples are shown in Table 3, where the outcomes from turbidity analysis are also shown for comparison purposes. Galligu concentration in the samples is estimated in the light of the proximity to the CDF obtained for a known galligu concentration. In table 3 the K-S index is compared with the benchmark values of know galligu concentrations (i.e. 0%. 50%, 100%). The lower the distance between CDFs, the closer the sample galligu content is to the one of the reference CDFs obtained in the calibration process. To illustrate our approach for determining galligu concentration through digital image analysis (Section 2.5.2.2), herein we are focusing on the results retrieved from the third runoff simulation test under fern ground cover (i.e. F1T3: fern 1, test 3; Fig.5.b). The CDF for F1T3 differed statistically from the CDFs obtained from the calibration process (Fig. 5a; Section 2.5.2.2). This suggested that the galligu concentration in F1T3 is neither 0 wt%, 50 wt% or 100 wt%. However, the CDF for F1T3 was closer to the CDF obtained for the prepared samples with a 50 wt% and 0 wt% concentration of galligu, suggesting that F1T3 could present a concentration between 0 wt% to 50 wt%. Since the distance is closest to CDF-50, we could assume that the galligu concentration in our example should be closer to 50%. This observation is further supported by the outcomes obtained from turbidity analysis, in which F1T3 showed a galligu concentration of 32 wt% (Table 3). The concentration of galligu for F1T3 can be also approached by comparing the image histograms directly (Fig. 5b). Yet, to have a better idea of the concentration of galligu in a given soil sample using this approach, we recommend the generation of CDFs for a larger array of galligu concentrations. Nonetheless, and in support to the goodness of our approach for determining the galligu concentration in the soil from digital image analysis, it is worth noting the similarity of the CDF for F1T12 and CDF-100 (Fig. 5d), which was not observed when comparing the histograms (Fig. 5c).

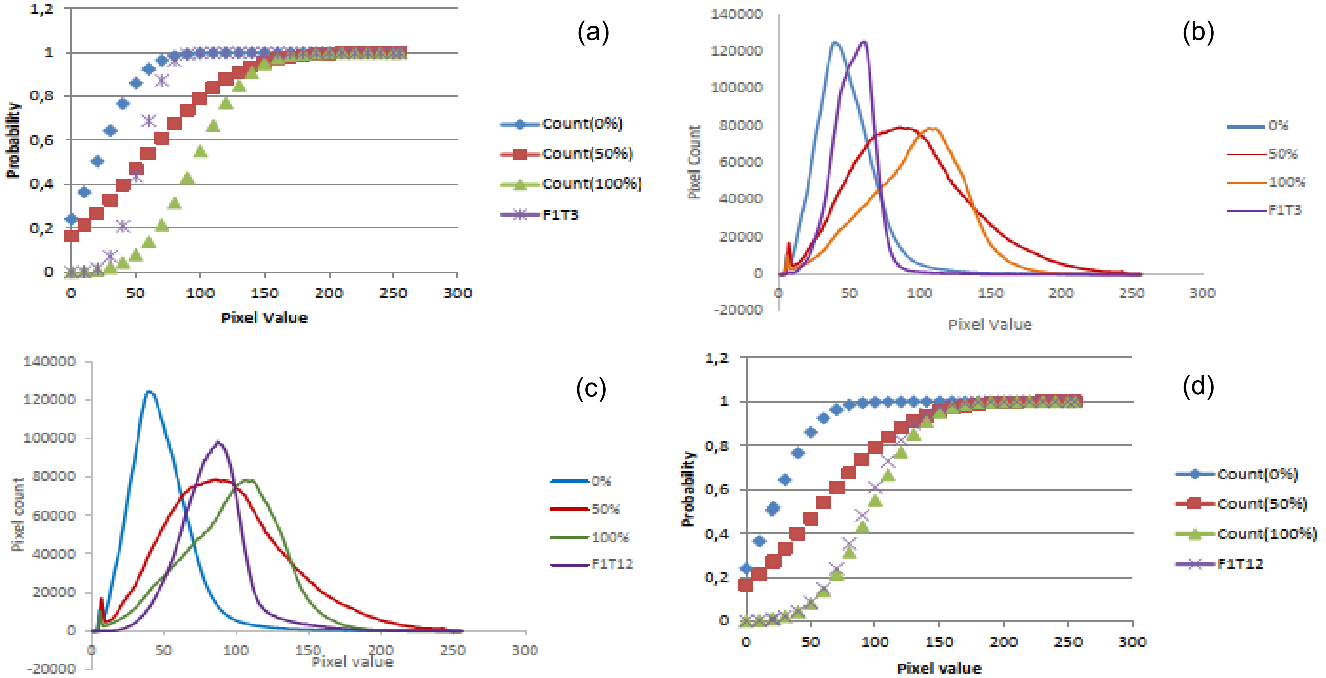

Figure 5(a). Cumulative Distribution Functions (CDFs) retrieved from the histograms belonging to the digital images from soil samples with known galligu concentration (i.e. 0%,50%, and 100%) and CDF for the simulation run F1T3 (fern cover 1 – simulation test 3).

(b) Histograms belonging to the digital images from soil samples containing known concentrations of galligu (i.e. 0 %, 50 %, 100 %) and for the simulation run F1T3 (fern 1 – simulation test 3).

(c)Histograms belonging to the digital images from soil samples containing known concentrations of galligu (i.e. 0 %, 50 %, 100 %) and for the simulation run F1T12 (fern 1 – simulation test 12).

(d) Cumulative Distribution Functions (CDFs) retrieved from the histograms belonging to the digital images from soil samples with known galligu concentration (i.e. 0%,50%, and 100%) and CDF for the simulation run F1T12 (fern cover 1 – simulation test 12).

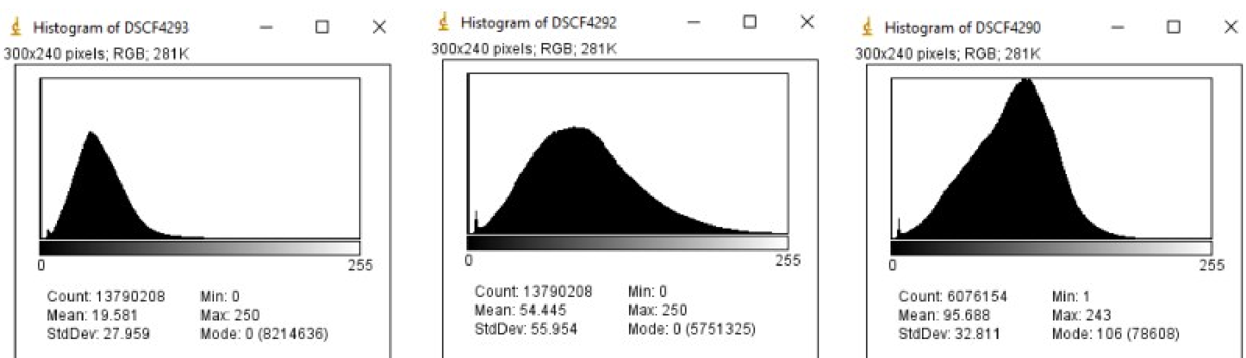

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Figure 6. Top: Illustration of the histograms retrieved from the digital images from three soil samples containing different concentrations of galligu; Bottom: digital images from three soil samples with different concentrations of galligu -i.e. 0 %, 50 % and 100 %, corresponding to the above histograms. The histograms with higher concentrations of the pollutant move closer to the right side where white/greyish pixels are. This comes from the colour of galligu particles compared with brownish soil grains. These were used in the calibration process to determine the concentration of galligu in the soil through digital image analysis.

Table 3. Kolomogorov-Smirnov (K-S) tests results from the comparison of the cumulative distribution functions (CDF) for the histograms belonging to the digital images for soil-galligu mixtures collected after rainfall simulation events. F: fern; A: alfalfa; U: unvegetated; T: simulation test number. Critical K-S index=0.120. *Galligu concentration in the samples is estimated in the light

of the proximity to the CDF obtained for a known galligu concentration (i.e. 0 %, 50 %, and 100 %) and compared with the results from the turbidity tests (Section 3.1.1).

Sample	Galligu concentration (%)			Galligu concentration range (%)*	Galligu concentration (%) from turbidity tests
	0	50	100		
	K-S Index				
F1T3	0.581	0.289	0.666	Between 0 % and 50 % - closer to 50 %	32
F1T8	0.609	0.261	0.503	Between 50 % and 100 % - closer to 50 %	16
F1T12	0.782	0.389	0.062	No statistical difference with 100 % CDF	20
F2T3	0.506	0.330	0.722	Between 0 % and 50 % - closer to 50 %	37
F2T8	0.311	0.233	0.619	Between 0 % and 50 % - closer to 50 %	33
F2T12	0.521	0.227	0.586	Between 0 % and 50 % - closer to 50 %	20
A1T3	0.533	0.302	0.686	Between 0 % and 50 % - closer to 50 %	33
A1T8	0.608	0.275	0.633	Between 0 % and 50 % - closer to 50 %	29
A1T12	0.175	0.514	0.883	Between 0 % and 50 % - closer to 50 %	31
U1T3	0.873	0.521	0.232	Between 50 % and 100 % - closer to 100 %	60
U1T8	0.493	0.163	0.442	Close to 50 %	47
U1T12	0.538	0.209	0.489	Close to 50 %	40
U2T3	0.678	0.285	0.169	Between 50 % and 100 % - closer to 100 %	83
U2T8	0.782	0.388	0.218	Between 50 % and 100 % - closer to 100 %	66
U2T12	0.820	0.428	0.125	Between 50 % and 100 % - closer to 100 %	70

The proposed approach to estimate the concentration of galligu in the soil through digital image analysis was able to correctly identify the concentration of galligu within the concentration range retrieved from turbidity tests (see Section 3.1.1) in 13 out of 15 samples (Table 3). However, only 8 of the 15 evaluated samples approached the CDFs retrieved from the calibration process satisfactorily (i.e. F1T3, F2T3, F2T8, G1T3, G1T8, U1T8, U1T12, U2T3;Table 3). For the remaining 5 samples (Table 3), it was required to assume the galligu concentration on the basis of the relative position of their CDFs with respect to the calibration CDFs (i.e. 0 wt%, 50 wt%, and 100 wt%; Fig. 6). These incongruities could be attributed to the quality of the digital image to proceed with such analysis, or the conditions in which the images were taken. Samples that are too wet were avoided, since this may have lehave d to high levels of light reflection, reducing the contrast between soil and galligu particles. It was also important to spread evenly the solids mixture as a thin layer, as thicker areas may covered smaller grains and particles and, thus, reducing the contrast between particles. The latter is evidenced by observing the images for samples F1T8 (i.e. fern 1 – simulation test 8) and F1T12 (i.e. fern 1 – simulation test 12) (Fig. 7), for which the results from the digital image analyses differed statistically from the outcomes from turbidity analysis (Table 3). As it can be observed in Fig. 9, the solids were not correctly spread on the aluminium disc (Section 2.5.2.2), leaving white spots or pale areas that have likely affected the results – i.e. the number of white pixels increased, likely due to presence of galligu particles and, as a result, this may have overestimated the concentration of galligu. Overall, the digital image analysis appeared to be more sensitive than turbidity tests, and it also constituted a good basis for the indirect estimation of the concentration of galligu in the soil.

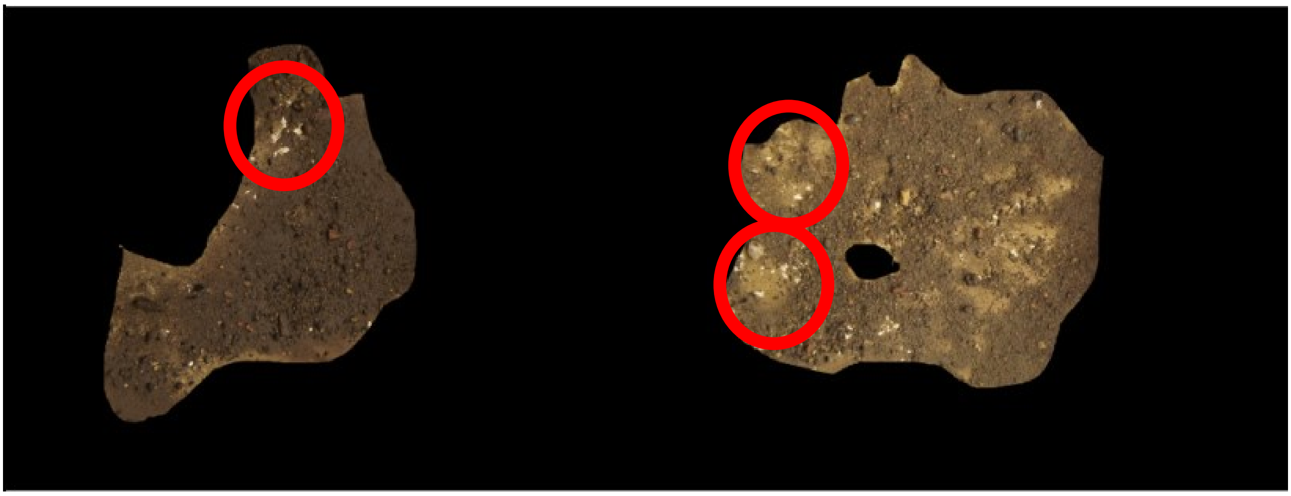

Figure 7 Digital images for the two soil-galligu samples – Left: F1T8 (fern 1 – simulation test 8); Right: F1T12 (fern 1 – simulation test 12). White spots and pale areas derive from an uneven spread of soil on the aluminium disc.

3.2. Phytostabilisation of galligu

3.2.1 Effect of vegetated ground cover on the axial transport of solids through runoff

The results from the axial transport tests under different ground covers (Section 2.3) are shown in Fig. 8. The results show that the amount of solids (i.e. galligu and soil) transported by runoff is the highest under fallow conditions and the lowest under alfalfa ground cover.

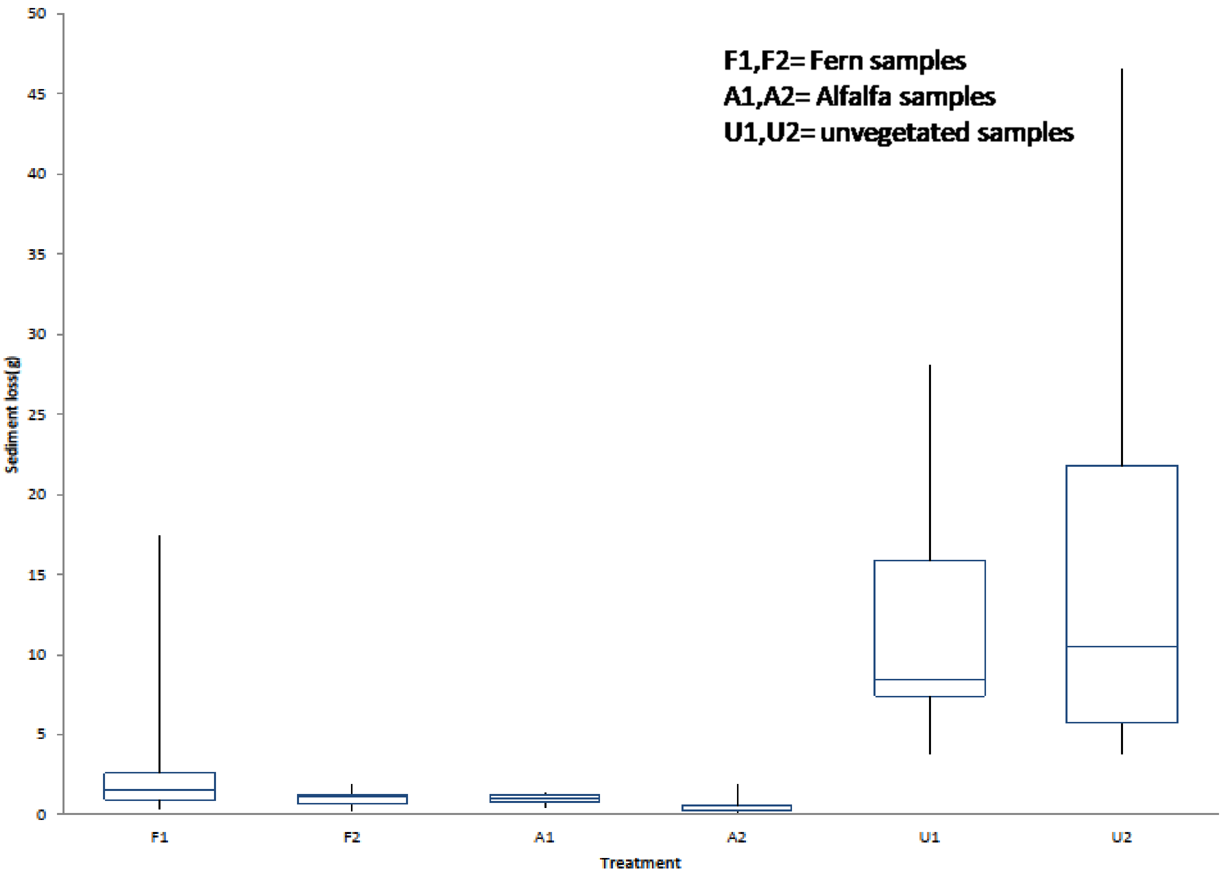

Fig. 8 Solids load in the runoff water under different ground covers; F-ferns, A-alfalfa, U-unvegetated.

Statistically significant differences in terms of solids retention were found between vegetated (F, A) and non-vegetated (U) ground covers (χ^2=50.43 df=5 p<0.01). This confirmed the effect of vegetation cover in reducing soil erosion through the increase in surface roughness (Thomsen, 2015). Furthermore, the results showed that alfalfa (A1, A2) was statistically more effective in solids retention than ferns (F1, F2) (χ^2=14.39 df=3 p<0.01). The average amount of solid loss in fallow samples was 161.5 g, while in ferns samples 26.08 g and alfalfa 8.77 g. It appeared that *Dryopteris affinis* was able to reduce the loss of solids by almost 84%, while alfalfa by 94% when compared to fallow soil conditions. These results are in agreement with previous research on sediment removal efficiency of vegetative strips (Gaharabaghi, et al., 2006). The better performance of alfalfa could probably be attributed to the more even and dense spread of the seeds over the axial soil columns compared to the axial columns vegetated with ferns. Ferns were established only on the central part of the axial soil column (Fig. 2), leaving the edges with no foliage or root cover which is the main action of plants in blocking solids runoff (Gonzalez-Ollauri and Mickovski, 2016; 2017b). In addition, the protective action to the soil surface against raindrop impact provided by the vegetation cover may have also led to the observed results (Thurow, 1997). In the treatments with ferns and alfalfa, the ground surface was partially protected by the aboveground foliage, which reduced the strength of the raindrops upon hitting the surface. The impact of each raindrop can break the soil aggregates and enhance the erosion and subsequent solid transportation (Vaezi et al., 2017).

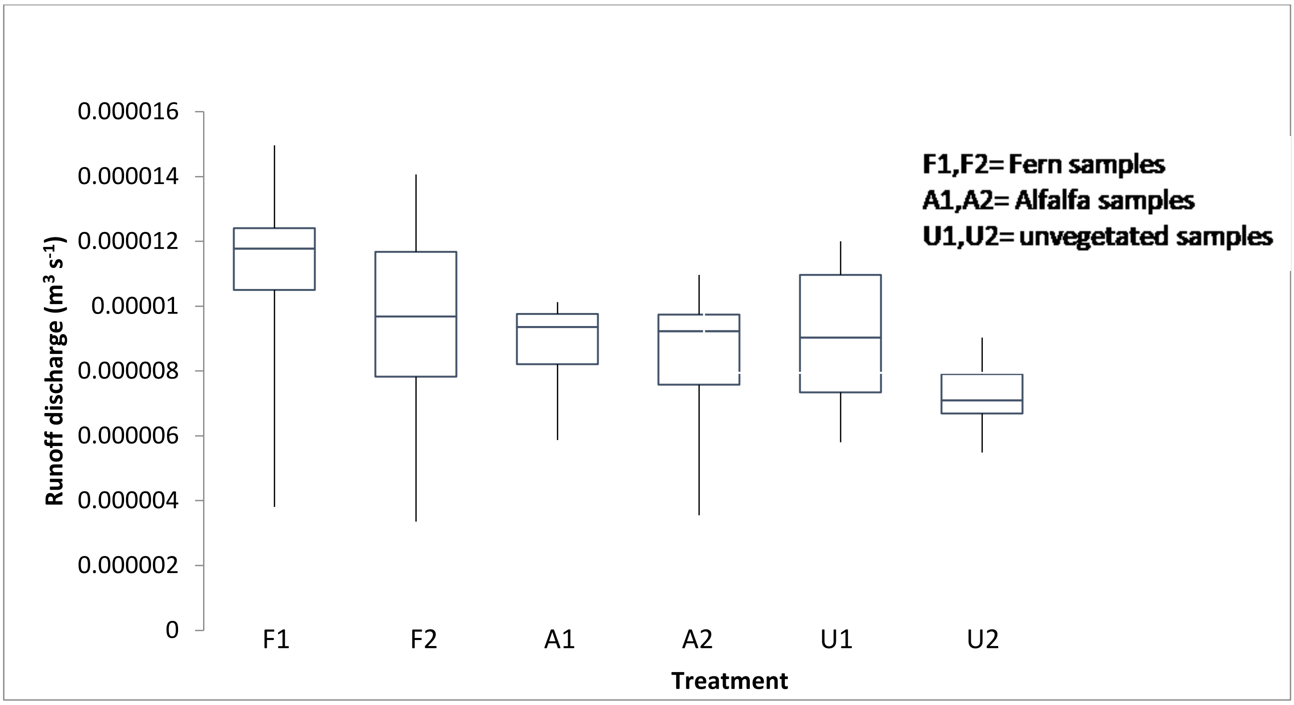

Fig. 9. Runoff discharge ($m^3\ s^{-1}$) for the three ground covers evaluated in this study (i.e. F-ferns, A-alfalfa, U-unvegetated).

The effect of vegetation on the water flux or discharge is shown in Figure 9. Counterintuitively, the runoff discharge was lower under fallow ground cover than under vegetated covers. The runoff discharge was statistically significantly different between ferns and fallow ground covers (χ^2 =7.5 df=3, p<0.01), with a lower discharge observed for the fallow treatment (Fig. 9). It is worth noting that the opposite result was expected (Queensland Government, 2015), since part of the runoff would have been captured by the leaves, percolated through the vadose zone, and be partially absorbed by the roots (Fazio, 2010). However, in our experiment, roots were not able to absorb water readily due to the briefness of the simulated rainfall events. Another possibility for our observations could be related with the lower mechanical strength (Gonzalez-Ollauri and Mickovski, 2017a) and aggregate stability (Shaoshan, 2010) of unvegetated soil following wetting-drying cycles. The latter can lead to the formation of cracks on the ground surface and, as a result, to the rapid infiltration of surface water and subsequent runoff amelioration. In fact, more cracks were observed under fallow soil conditions. It is worth noting that the formation of cracks may be fostered by the high pH (i.e. 12.06) observed in the soil-galligu mixtures (Santonoceto, 2015), which could be also responsible for the poor development of a vegetation cover observed in our experiments (Santonoceto, 2015). Anyhow, our simulation runs were undertaken when the soil columns were water saturated or nearly saturated, which limits the amount of water that infiltrates in the soil and encourages the formation of runoff (Green and Ampt, 1974; Penna, 2011). Accordingly, it is also plausible that under vegetated conditions, the soil may retain more water than under fallow conditions (e.g. Manisha, 2011) as a result of different mechanisms influenced by the plant cover – e.g. shading and cooling of the ground surface, alteration of the turbulence patterns atop the ground surface, creation of physical structures that concentrate water, and facilitation of percolation towards deeper soil layers (Shaxson & Barber, 2003). However, in spite of the observations described above, no statistically significant differences in terms of water runoff were observed between fern, alfalfa and the fallow ground covers (χ^2 =10.05 df=5 p>0.01).

3.2.2. Effect of vegetated ground cover on the axial transport of galligu through runoff

Vegetation ground covers proved to be effective in the retention of galligu in the soil (Figure 10). We found a statistically significantly higher concentration of galligu in the runoff generated under fallow soil conditions ($\chi2$=21.5731; df=5; p<0.01; Fig. 10) than under vegetated conditions. This result suggested that the root systems were able to trap galligu particles and prevent them from being washed down with the runoff produced after the simulation of rainfall (Section 2.3). On average, ferns were able to reduce galligu in the runoff by 59%, while alfalfa by 62%. The difference between the two vegetated groundcovers (i.e. fern and alfalfa) could have its origin in the topological differences of the root systems between the two evaluated species. Alfalfa tends to develop a dense and deep root system with abundant adventitious roots compared to ferns, which tend to have many fine fibrous roots. This difference could make alfalfa more effective to trap solid contaminants in the soil (Samac, 2007).

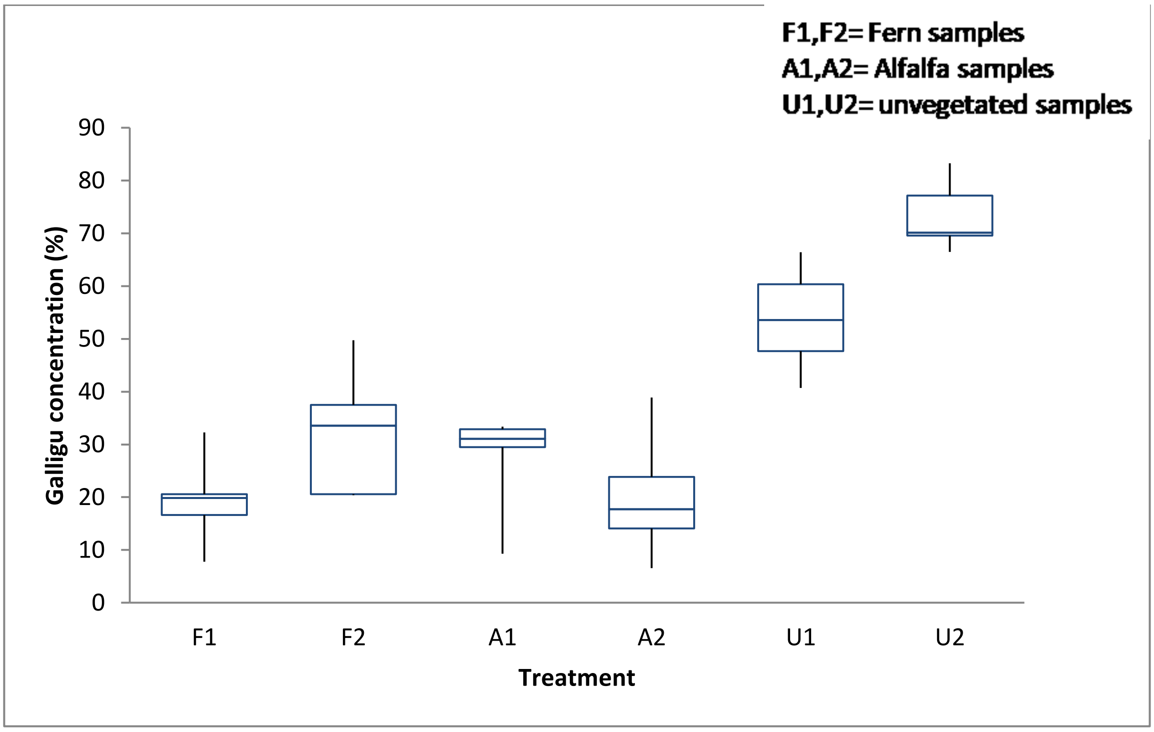

Figure 10 Galligu concentration (in %) in the runoff collected after the series of rainfall simulation events under different ground covers (F: fern; A: alfalfa; U: fallow).

3.2.3 Effect of vegetated ground cover on water percolation

The results from the tests evaluating the vertical transport of galligu though percolation (Section 2.4; Fig. 13) confirmed that vegetated soils have, in general, better drainage conditions than fallow soils (e.g. Istanbulluoglu, 2005). Vegetation roots may lead to the formation of macro-pores (Ahmed, et al., 2015; Lange, et al., 2008), thus encouraging percolation and the potential transportation of galligu down the soil profile. In our experiment, however, we observed an anomalous behaviour in two vegetated samples (i.e. Fern FV1 and alfalfa AV3; Fig. 11). Here, a substantially lower infiltration was measured when compared to fallow soil conditions (Figure 11). More compacted soils tend to not change their textural porosity but tend to be characterised by relict structural pores accessible only through micro-pores of the soil matrix, which could result in a change of the soil hydraulic properties (Richard, et al., 2001). A possible explanation for these results could lie in the natural variability between treatments for which a bigger number of repeats would be necessary. Additionally, this variability and uncertainty could have been induced by the use of a stopwatch and visual observation to determine the percolation time.

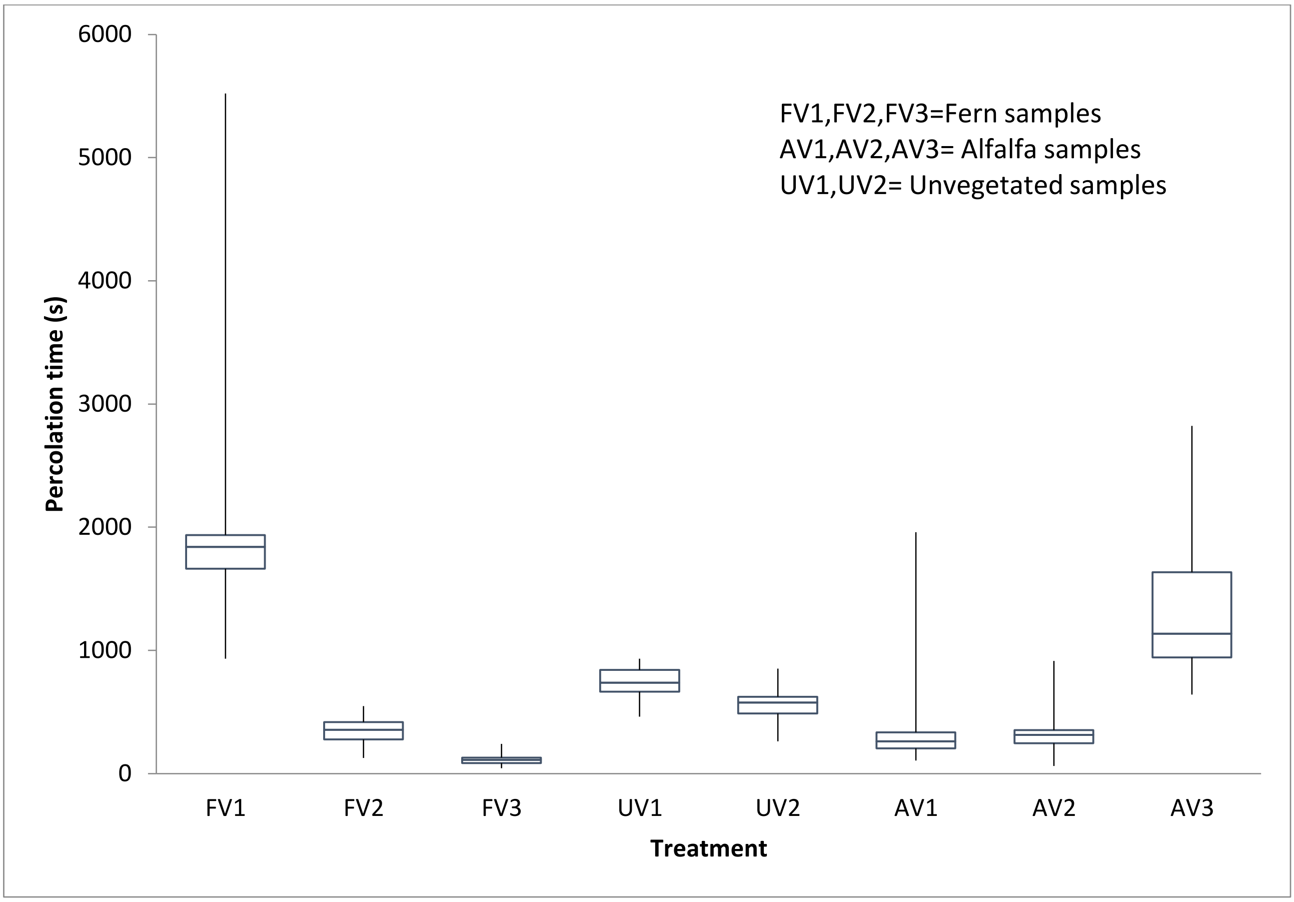

Figure 11 Percolation time for the different ground covers established in the percolation tests (see Section 2.4.2) of this study – i.e. FV: fern; UV: unvegetated; AV: alfalfa.

3.2.4 Effect of vegetated ground cover on the vertical transport of galligu through percolation

With regard to the assessment of the vertical transport of galligu under different ground covers (Section 2.4; Fig. 12), the results suggest that vegetation could contribute to the transport of galligu in depth along the soil column. Although no statistically significant differences were found between vegetated and fallow ground covers (χ^2=5.96; df=7; p>0.05), our observations indicate that the devised methodology could be used to assess the vertical movement of galligu within the soil under different ground covers.

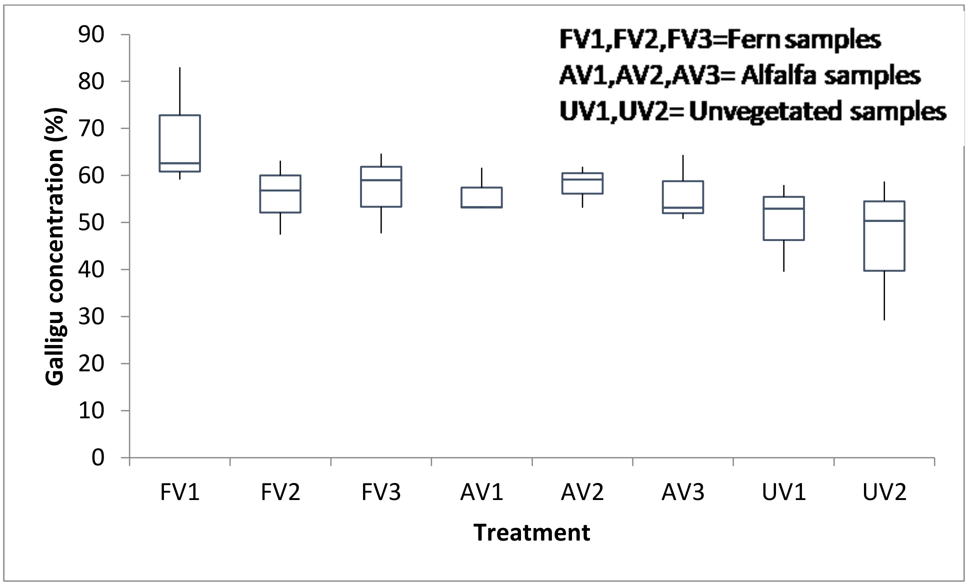

Figure 12 Galligu concentration (%) at three different soil column depths (i.e. 1: Top, 2: Middle; and 3: Bottom) and under different ground covers –i.e. F: Fern; AV: Alfalfa; UV: Fallow.

In the vegetated treatments, galligu appeared to be equally spread in all the three soil depths evaluated (i.e. 50 mm, 100 mm, 150 mm; Fig. 13). The fallow treatments, however, showed a deficit of galligu in the bottom layer when compared to the vegetated ground covers (Fig. 12). This was evidenced by measuring the length of the polluted zone at the end of the rainfall simulation tests (see Section 2.4.2). Under the fern cover, the limit between polluted and unpolluted sections appeared deeper in the soil column compared to the other ground covers tested herein. This may be related to the length of the fern roots, which were longer than the alfalfa roots. As a result, deeper preferential flow paths could have appeared in the soil column vegetated with ferns (Wildenschld,1994), which could have allowed the particles of galligu to move down the soil column through the macro-pores created by the root systems (Bodner,2014). This could be regarded as a negative effect of vegetation in the stabilisation of galligu. The downward movement galligu might constitute a hazard to the contamination of groundwater reservoirs.

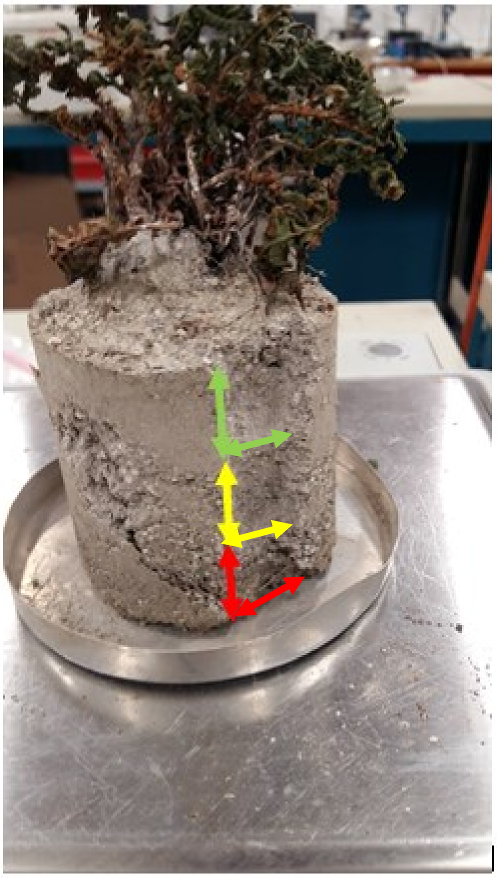

Figure 13 Illustration of the zones sampled within the vertical soil columns to evaluate the vertical movement of galligu –i.e. Top (green), middle (yellow), bottom (red).

4. Conclusion

Vegetation was able to reduce the transport of solids (i.e. soil and galligu) axially with respect to fallow soil following the simulation of heavy rainfall events. Accordingly, vegetation effectively limited the runoff of galligu, with alfalfa being the most effective ground cover. Our observations suggest that phytostabilisation with ferns and alfalfa can be an effective method to reduce the mobilisation of galligu through runoff. However, vegetation fostered the vertical transportation of galligu in the soil column, where alfalfa showed a greater retention capacity. Yet, it must be noted that alfalfa did not reach maturity in the course of this study. We recommend the replication of the experiment described herein with fully grown plants to assess whether there are any significant changes in the percolation of galligu.

Turbidity and image-based analyses were confirmed as viable methods to estimate the concentration of galligu within the soil. However, we encourage further investigation to define more accurate protocols aiming at quantifying the concentration of galligu in the soil accurately, as with the suggested approaches we were only able to distinguish the potential range of galligu concentration in the soil. Undoubtedly, the original approaches elaborated herein to estimate the concentration of galligu in the soil provide a good basis for further work focusing on polluted soil by solid contaminants and to apply the resulting knowledge into the sustainable remediation of polluted soils with vegetation.

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