Chemosphere, Volume 107, July 2014, Pages 43-50,
DOI:10.1016/j.chemosphere.2014.03.035

Influence and interactions of multi-factors on the bioavailability of PAHs in compost amended contaminated soils

Guozhong Wu [a,b,c], Xingang Li [b,d], Cédric Kechavarzi [a], Ruben Sakrabani [a], Hong Sui [b,d], Frédéric Coulon [a,e] *

[a] Department of Environmental Science and Technology, Cranfield University, Cranfield MK43 0AL, UK

[b] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

[c] Division of Ocean Science and Technology, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

[d] National Engineering Research Centre for Distillation Technology, Tianjin 300072, China

[e] Centre for Research in Environmental, Coastal and Hydrological Engineering, School of Civil Engineering, Surveying and Construction, University of KwaZulu-Natal, Howard College Campus, Durban, 4041, South Africa

* Corresponding author:

E-mail: f.coulon@cranfield.ac.uk

Phone: +44 1234 754 981

Fax: +44 1234 751 036

Abstract

Compost amendment to contaminated soils is a potential approach for waste recycling and soil remediation. The relative importance and interactions of multiple factors on PAH bioavailability in soils were investigated using conjoint analysis and five-way analysis of variance. Results indicated that soil type and contact time were the two most significant factors influencing the PAH bioavailability in amended soils. The other two factors (compost type and ratio of compost addition) were less important but their interactions with other factors were significant. Specifically the 4-factor interactions showed that compost addition stimulated the degradation of high molecular PAHs at the initial stage (3 month) by enhancing the competitive sorption within PAH groups. Such findings suggest that a realistic decision-making towards hydrocarbon bioavailability assessment should consider interactions among various factors. Further to this, this study demonstrated that compost amendment can enhance the removal of recalcitrant hydrocarbons such as PAHs in contaminated soils.

Keywords: Compost; Bioavailability; PAH; Conjoint analysis; Interactions

1. Introduction

Adding compost into contaminated soils is an effective management approach to reusing waste and remediating soils (Semple et al., 2001; Namkoong et al., 2002; Reid et al., 2002; Puglisi et al., 2007; Sayara et al., 2010). The success or failure of this approach for soil remediation is determined by the bioavailability of toxic compounds such as polycyclic aromatic hydrocarbons (PAHs) instead of the total concentration of petroleum hydrocarbons (Semple et al., 2001; Latawiec et al., 2011), as the latter will lead to an over-estimation of risks (Kördel et al., 2013). It is known that bioavailability depends on the mass transfer rate and the intrinsic activity of cell (Semple et al., 2003). These processes are influenced by a number of factors including soil organic matter (SOM) and inorganic constituents, properties of contaminants, and soil processing by microorganisms (Reid et al., 2000). Although several studies acknowledged it is of special interest to know to what extent physicochemical factors influence PAHs bioavailability during bioremediation (Semple et al., 2001; Puglisi et al., 2007; Sayara et al., 2010; Wu et al., 2013a), the quantitative comparison of the influence of these factors is still rare, which makes difficult to select operational conditions such as the ratio of compost application.

To handle such cases where multiple physicochemical factors influence the choice of the process, conjoint analysis (CJ) can help to better inform the decision-making design stage. CJ has been defined as any decomposition method that estimates the structure of a consumer’s preferences, given his or her overall evaluations of a set of alternatives that are pre-specified in terms of levels of different factors (Green and Srinivasan, 1990). In general, the researchers use a combination of different factors to generate a number of cards (or questionnaires) that are used to describe the potential of a product, which are then presented to the subjects who are asked to rank the cards based on their overall evaluation of the product. CJ method determines the influence of each feature and how it contributes to the overall judgment of the subjects. Tremendous progress have been made in the past 30 years refining CJ method to decision-making for new product evaluation, competitive or product positioning analysis and market segmentation (Lohrke et al., 2010). However, CJ is relatively new in the evaluation of environmental processes where only a few scattered examples have been reported (Lareau and Rae, 1989; Mackenzie and Eduljee, 1990; Gan, 1992; Opaluch et al., 1993; Roe et al., 1996; Johnson and Desvousges, 1997; Adamowicz et al., 1998; Farber and Griner, 2000; Álvarez-Farizo and Hanley, 2002; Muramatsu and Nakamura, 2002; Cheung and Chung, 2008). To the best of our knowledge, there is no yet any application of CJ to evaluate the influence of multiple physicochemical factors on hydrocarbons bioavailability in contaminated soils.

The rather slow development in environmental applications is somewhat surprising, which is attributed to some drawbacks in practice. One potential pitfall is the design and implementation for data collection by social survey in this method. Selection of performance indicators and participants is expert-driven and therefore is the main challenge (Alriksson and Öberg, 2008). Results may be influenced from cognitive and contextual biases which reduced the repeatability (Gregory et al., 1993). There is always a risk of self-selection bias when respondents with a strong opinion on the subject volunteer to participate (McCoullough, 2002). However, such drawback can be circumvented in this study because the data used are obtained from duplicate solvent extraction experiments in the laboratory instead of social survey.

Although a number of factors influencing bioavailability have been identified, the role of each factor on bioavailability was often investigated separately without comprehensive understanding the interactions. This is likely to limit the predictability of end points associated the bioremediation of PAHs when evaluating its viability for soil remediation (Ortega-Calvo et al., 2013). Only a few studies have showed the influences of mixture-contaminant interactions on bioavailability. For example, Bamforth and Singleton (2005) found that co-contaminants such as BTEX (i.e. benzene, toluene, ethylene, and xylene) compounds and aliphatic hydrocarbons, which were readily biodegradable in situ, hindered the biodegradation of PAHs by the depletion of available oxygen. Sandrin and Maier (2003) further demonstrated that the presence of heavy metals decreased the bioavailability of organic contaminants as they were impacting both the physiology and ecology of organic degrading microorganisms. Couling et al. (2010) observed that the presence of multiple PAH-mixture reduced the bioavailability of the more readily degradable (or low molecular weight, LMW) PAHs by competitive inhibition of the enzymes associated with biodegradation, but increased the bioavailability of those usually more recalcitrant (or high molecular weight, HMW) PAHs by producing inducible enzymes for catabolism. However, the interactions within PAH groups have not been adequately defined. Most of the studies have used artificially spiked samples instead of authentic contaminated soils while the real-world circumstances might be more complex (Latawiec et al., 2011). Moreover, the compost addition would further increase the complexity of these interactions by changing soil properties, nutrient availability and the retention of contaminants (Briceno et al., 2007). For instance, some studies reported that an inappropriate ratio of compost addition may retard or inhibit microbial activity and bioavailability (Thomas et al., 1992; Namkoong et al., 2002). In contrast, Puglisi et al (2007) observed no difference in phenanthrene bioavailability when 10 or 30 tha^{-1} of compost was added to the soil. These divergent findings may be attributed to the fact that the multiple interactions were not taken into account in these studies. The knowledge on multiple factor interactions would contribute to make a more informed picture of the magnitude of each factor influence and interaction.

Our recent study demonstrated the coexistence of sorption, desorption and degradation of PAHs in the contaminated soils after compost addition (Wu et al., 2013a). The contribution of these processes to the PAH loss was evaluated by analysing the changes in the total and bioavailable concentration during incubation. In this study, we applied CJ and multi-way ANOVA to (i) identify the influence of selected physicochemical factors including soil type, compost type, application ratio, and contact time on the bioavailability of 16 PAHs, and (ii) quantify the intricate interactions among these factors.

2. Methodology

2.1 Data collection

An eight-month microcosm experiment was carried out using three contaminated soils amended with either green or meat compost at two ratios (250 and 750 t ha^{-1}) as described in Wu et al. (2013a). Briefly, soil A was a sandy loam soil spiked with diesel at 12.5 g kg^{-1} and soil B and C were two genuinely contaminated soils with coal tar and coal ash, respectively. The compost amendment, incubation process and the determination of total and bioavailable concentration of PAHs were detailed in our previous studies (Wu et al., 2013a; Wu et al., 2013b; Fig SM-1 and SM-2). The bioavailable concentrations of 16 PAHs including acenaphthene (Ace), acenaphthylene (Acy), naphthalene (Nap), anthracene (Ant), 2-bromonaphthalene (BNap), phenanthrene (Phe), fluorene (Flu), fluoranthene (FL), chrysene (Chr), pyrene (Pyr), benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[ghi]perylene (BgP), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DbA) and indeno[1,2,3-cd]pyrene (InP) were used in the conjoint analysis. The percentage loss of bioavailable concentration during the incubation process was used in the analysis of factor interactions.

2.2 Conjoint analysis

The first step concerns the identification of factors as significant predictors of utility, assignment of levels to factors, and subjects of the investigation. PAH bioavailability in soil amended with compost is influenced by several factors such as temperature, water content, ageing time, SOM, nutrients content and the amount of compost added. Some of these factors can be categorised into groups; for example, pH, SOM, moisture content and particle size are the physicochemical properties of soil which vary between different soil types. Additionally, the number of factors should not be too large; otherwise too much information would have to be handled simultaneously during each analysis. Therefore, four factors with corresponding levels in parentheses were selected including (i) soil type (soil A, B, and C), (ii) compost type (green compost, meat compost), (iii) ratio of compost to soil (250 and 750 t ha^{-1}) and (iv) incubation time (3, 6 and 8 months). Subjects ‘participated’ in the experiments were the 16 PAHs instead of human beings in this study.

In the second step of CJ, the profiles (combination of factors) were set up using the orthogonal design instead of full factorial design because of its great advantage in terms of experimental time and cost (Peace, 1993). For each PAH, 16 profiles were generated via orthogonal array by running the Generate Orthogonal Design procedure using SPSS and 5 profiles (holdout profiles) were randomly selected (Table 1). A total of 256 profiles (16 profiles × 16 PAHs) were used for evaluating the part-worth values of the factors. The holdout profiles, not used for part-worth estimation, were used to examine the goodness-of-fit of the CJ models. The part-worth is a parameter associated with each level of a factor. Large part-worth value is assigned to the most preferred level and small part-worth is assigned to the least preferred level. Part-worth of each level (P_i) was calculated as follows:

$$P_i = (\bar{r}_i - \bar{r}_0) \cdot \sqrt{n_{all} \Big/ \sum_{j=1}^{n_{all}} (\bar{r}_j - \bar{r}_0)^2}$$

where n_{all} is the number of levels across all factors which was equal to 10 in this study, $\bar{r}_0$ is the overall mean ranking which was equal to $(1+2+3+...+16)/16 = 8.5$, $\bar{r}_i$ represents the average ranking for each level of the factor. A positive value of part-worth suggested a lower bioavailable concentration. For the factors with only two levels, the part-worth values of each level should be of the same magnitude but with opposite signs, as each level in a factor appears the same times according to orthogonal design (e.g. green compost and meat compost appears 8 times, respectively, in the 16 profiles shown in Table 1 excluding the holdout profiles) and

$$(\bar{r}_1 - \bar{r}_0) + (\bar{r}_2 - \bar{r}_0) = \bar{r}_1 + \bar{r}_2 - 2\bar{r}_0 = \frac{(1+2+3+...+16)}{8} - 2\bar{r}_0 = 0.$$

Subsequently, the utility for a particular profile can be determined by adding up the part-worth of the levels of factors involved in this profile. The optimal profile with the greatest mean utility of dependent variable is selected and the associated values of the independent variables are determined as the optimal condition. Finally, the relative importance (RI) of each factor can be calculated as follows:

$$RI = R_i \Big/ \sum R_i$$

where R_i is the range of part-worth that equals the difference between the lowest and highest part-worth across all levels of a factor.

In order to examine the accuracy of the CJ model for predicting the ranking of the profiles in terms of PAH bioavailability, the part-worth values were used to predict the ranking of bioavailable concentration in the 5-holdout profiles. The correlation between the actual rank and the predicted rank was evaluated by calculating the Pearson's R and Kendall's tau correlation coefficients, which were then used to test the model validity and the reliability of the original estimates. These two coefficients were expected to be close to 1 if the utility of profiles was successfully estimated by the part-worth values and consequently it was reliable to assess the relative importance of each factor for the PAH bioavailability changes using CJ method.

2.3 Five-way ANOVA

The strength of complex interactions between the impact factors including soil (S), compost (C), ratio (R), time (T) and the number of benzene rings in PAH compounds (P) were detected, estimated and quantified using five-way ANOVA technique. The calculated factor interactions were visualized using contour plots, which are graphical techniques for representing a three-dimensional surface by plotting constant z-slices called contours, on a two dimensional format. That is, given a value for z, lines are drawn for connecting the (x, y) coordinates where that z value occurs (Bradley, 2007).

3. Results and discussion

3.1 Significance of impact factors

Fig. 1 indicated that majority of the bioavailable concentration in the designed profiles was below 3 mg kg^{-1} and the highest bioavailable PAH concentrations were observed in Profile 9 (Soil B, green compost, 750 t/ha, and 3 months) and Profile 10 (Soil B, meat compost, 750 t/ha, and 3 months). The bioavailable PAHs in Profiles 1-8 was obviously less than that in the remaining profiles as the initial total PAH concentration in Soil A was one order of magnitude lower than that in the other two soils (Fig. SM-1 in the Supplementary Materials (SM)). The ranking profiles for each PAH (Table SM-1) were used to calculate the part-worth values of each level of the factors as shown in Fig. 2.

Both the range and average of part-worth values for Soil A were the highest among the three soils (Fig. 2), which indicated that PAH bioavailability was most susceptible to decrease in Soil A. This might be attributed to the weaker binding of PAHs with soils due to the much less organic carbon content in the spiked soil (3%) than in the other two genuinely contaminated soils (17%) (Wu et al., 2013a). The reduced bioavailable PAHs in Soil A was mainly transformed into the sorbed fractions, which resulted in the decreased percentage of bioavailable fractions in the total concentration especially at the initial stage of incubation (Fig. SM-2). Neither the type nor the ratio of compost was important for bioavailability as the corresponding average part-worth values were close to zero (Fig. 2). This was further confirmed by the estimated relative importance of each influence factor for the bioavailability of both individual PAHs and overall samples (Fig. 3). Results indicated that the least factors influencing bioavailability were compost type and the ratio (< 10%), which corroborated the work of Puglisi et al. (2007). The soil type and incubation time were characterised as the two factors determinant in the PAH bioavailability, which contributed to 52% and 40% to the overall influences, respectively (Fig. 3). Particularly, the contribution of time to the bioavailability changes was less marked for HMW PAHs than LMW PAHs (e.g. NaP, Acy, BNap and Ace), suggesting greater degree of bioavailability decrease in the LMW PAHs during incubation process. This was consistent with previous study, which indicated that the leaching and volatilisation processes being responsible for bioavailability changes of LMW PAHs were more time dependent while the recalcitrant nature of HMW PAHs made them less susceptible to incubation time (Wu et al., 2013b).

The Pearson's R and Kendall's tau coefficients were 0.996 and 0.867, respectively, along with significance ("p" probability value) of 0.001. These statistics were highly significant, therefore, we concluded that (i) there was a high level of correlation between the observed and estimated ranks of PAH bioavailability, and (ii) the estimation of the relative importance of each factor aforementioned was reliable based on the data of PAH bioavailable concentration in the orthogonal designed profiles.

3.2 Interactions among impact factors

Results indicated that the main effects of all the factors were significant at the confidence level of 95% (Table 2). Generally, the bioavailability decrease was negatively correlated with the number of aromatic rings (Fig. SM-3). This could be attributed to the greater stability with higher numbers of aromatic rings which reduce the lability of carbon to soil microbes and hence reducing bioavailability. The potentially stronger sorption of HMW PAHs also contributed to the observed negative correlation. The compost type had the least significant influence ($P = 0.042$). The loss of bioavailable PAHs was obviously enhanced by adding compost (Fig. SM-1) but insignificant difference was observed between the two doses of compost. This was consistent with the findings from conjoint analysis (Fig. 2) as the form of CJ model resembles ANOVA or standard regression equation that investigated dependence relationships by minimizing the error between actual and estimated values (Lohrke et al., 2010). Compared with ANOVA, CJ method is unique in that (i) it can be used to examine at both the individual and overall levels (Fig. 3), and (ii) it allows each influence factor to have a different relationship (e.g. linear and quadratic) with the dependent variables while ANOVA requires all factors to have the same one (e.g. linear), which makes it more flexible when dealing with complex decision-making issues (Hair, 2006). However, the CJ method in this study did not incorporate the interaction section and the interpretation of the multiple factors experiments on the main effects alone is incomplete, as it is based only on the mean of each factor and ignores the interactions within the factors affecting the outcome.

The five-way ANOVA results regarding the significance of the 2-factor, 3-factor and 4-factor interactions on PAH bioavailability changes are presented in Table 2. All 2-factor interactions except three of them (T×C;C×R; C×P) and all 3-factor interactions with exception of four of them (T×C×R;T× C×P;S×C×R;C×R×P) were significant at $\alpha = 0.05$. Of the five possible 4-factor interactions, T×S×C×P, T×S×R×P, and S×C×R×P were significant ($P < 0.05$).

In order to gain insights into the process, the 2-factor interaction plots are presented in Fig. 4, where the non-parallel lines in the plot matrix identify an interaction. The greater the lines depart from parallel, the greater the degree of the interaction is. This means the changes in the level of one factor would change the effect of the other factor on the outcome. On contrary, there is unlikely to be a significant interaction if the lines are parallel (e.g. second column of the plots for compost × ratio (C×R), compost × time (C×T) and compost × PAH (C×P)).In such cases, the two-factor interaction graph just reflects the main effect of either factor. For example, the fact that the line for 0 t ha^{-1} is lower than for 250 and 750 t ha^{-1} suggested that compost addition generally resulted in lower bioavailability than blank soils, while such trends would not vary by changing the type of compost as there was no interactions between the type and the ratio of compost (Fig. 4e).

Explanation of the plots for 2-factor and 3-factor (plots not shown) interactions will not be detailed, because a rule of thumb in statistics is that the evaluation of a multi-factor ANOVA should start with the highest order relatives before examining the lower order factor interactions (Madurantakam et al., 2009). This means to firstly interpret the most complicated interactions, if it can be dismissed, then successively less complicated interactions. In this study, the highest order factor interactions that were significant involved four factors, which represented the most complete explanation of the observed effects (Table 2). Since there are four factors, each time two factors will be hold at a constant level when plotting the other two factors. The results change when the holding levels are changed. All the possible 4-factor interactions are graphically visualised in Fig. 5. One of such interactions (T×P×S×R, Fig. 5e) is explained in detail as illustrative purpose.

The main finding of Fig. 5e was the different behaviour of HMW (5- and 6-ring) PAHs at the initial stage of incubation (bottom right corner of the contour plots). The loss of bioavailable HMW PAHs after compost addition in Soil C was obviously greater than that in the other two soils, irrespective of the type and ratio of compost added. The similar phenomenon was observed in Figs. 5a and d. This might be attributed to the higher naphthalene concentration in Soil C (2.9 mg kg^{-1}) than in Soils A (0.1 mg kg^{-1}) and B (0.6 mg kg^{-1}), as previous studies demonstrated that naphthalene or naphthalene-like intermediates stimulated the degradability of PAHs with greater ring number (Barnsley, 1983; Eaton and Chapman, 1992; Couling et al., 2010).

Another possible explanation was the competitive sorption within PAH groups, which has been previously reported to decrease the sorption of HMW PAHs and thereby increase the bioavailability (Stuart et al., 1991; White et al., 1999). However, little difference was found in the loss of bioavailable HMW PAHs among the three unamended soils (i.e. no obvious colour gradient at bottom right of the contour plots in Fig. 5e). This implied that the competitive sorption might be enhanced by compost addition. This encouraged the use of compost amendment strategy for enhancing biotransformation of the relatively more recalcitrant residual oil, because the prospective innovation should be targeted at reducing the bound fractions of contaminants rather than only removing the rapidly desorbed fractions of PAHs (Ortega-Calvo et al., 2013).

Another factor attributable for the reduced loss of the bioavailable HMW PAHs in Soil A and B compared to Soil C at the initial stage was the difference in soil texture. Soil A and B had larger percentage of sand (pore size: 2000 μm-50 μm) but less proportion of silt (pore size: 50 μm - 2 μm) than Soil C (Wu et al., 2013a). A reduction of large sand pores upon compost addition was supposed to occur in Soil A and B as Cox et al. (2001) showed that the amended solid compost cemented and aggregated together with soil particles blocking the large soil pores. This would increase the difficulties for the PAHs initially entrapped in the pores to expose to the microorganisms, which resulted in less extent of degradation at expense of bioavailable fractions in Soil A and B compared with Soil C.

The overall results of this study highlighted the demand for taking into account multi-factor interactions during bioavailability assessment. Although the ratio and the type of compost amendment had little influence on PAHs bioavailability, the influences of their interactions with other factors were significant. Pilot scale testing needs to be carried out before reaching a definitive conclusion on the optimal (if any) ratio of compost application, because mixing plenty of non-contaminated compost with contaminated soil will result in a far greater quantity of contaminated material (Semple et al., 2001) unless the composted soils are proved to meet the PAS100:2011 or the Composting Association standards (BSI, 2011). Composted materials which do not comply with the standards will be regulated - either be still treated as a 'waste' by the UK EPA and therefore subject to UK Wastes Management Licensing Regulation (Lord et al., 2007), or be under exemption (e.g. Paragraph 9 Exemption for "The reclamation or improvement of land" (SEPA, 2011)).

4. Conclusion

The overall relative importance of soil, compost, ratio of compost to soil, and contact time to the PAHs bioavailability in the compost amended soils was 52%, 3%, 5% and 40%, respectively. Compared with soil type, contact time was generally more important to the LMW PAHs but less important to the HMW PAHs. Although the main effects of compost type and ratio of compost addition were insignificant, their interactions with other factors were significant. Interpretation of the 4-factor interactions showed that the compost amendment potentially enhanced the biotransformation of the relatively more recalcitrant PAH fractions by changing the PAH-soil interactions such as competitive sorption during the initial stage of incubation. To the best of our knowledge, this is the first study to investigate the multiple interactions in the soil-compost-PAH system regarding PAH bioavailability especially in the genuinely contaminated soils. The overall results revealed the importance of soil and time for bioavailability change and reinforced the incorporation of multi-factor interactions into risk assessment for bioremediation.

Acknowledgements

This research was supported by the Engineering Physical Science Research Council (EPSRC) and Waste Resource Action Programme (WRAP) (Life III Environment programme; No. OBF009), the National Natural Science Foundation of China (No. 21307069), Guangdong Natural Science Foundation (No. S2013040012413).

Reference

Adamowicz, W., Boxall, P., Williams, M., Louviere, J., 1998. Stated preference approaches for measuring passive use values: choice experiments and contingent valuation. Am. J. Agr. Econ. 80, 64-75.

Alriksson, S., Öberg, T., 2008. Conjoint analysis for environmental evaluation: A review of methods and applications. Environ. Sci. Pollut. R 15, 244-257.

Álvarez-Farizo, B., Hanley, N., 2002. Using conjoint analysis to quantify public preferences over the environmental impacts of wind farms. An example from Spain. Energ. Policy 30, 107-116.

Bamforth, S.M., Singleton, I., 2005. Bioremediation of polycyclic aromatic hydrocarbons: current knowledge and future directions. J. Chem. Technol. Biot. 80, 723-736.

Barnsley, E., 1983. Bacterial oxidation of naphthalene and phenanthrene. J. Bacteriol. 153, 1069-1071.

Bradley, N., 2007. The Response Surface Methodology. Msc Thesis. Indiana University South Bend.

Briceno, G., Palma, G., Duran, N., 2007. Influence of organic amendment on the biodegradation and movement of pesticides. Crit. Rev. Env. Sci. Tec 37, 233-271.

BSI, 2011. PAS100: 2011 Specification for composted materials, British Standards Institution, London, UK.

Cheung, H.D., Chung, T.M., 2008. A study on subjective preference to daylit residential indoor environment using conjoint analysis. Build. Environ. 43, 2101-2111.

Couling, N.R., Towell, M.G., Semple, K.T., 2010. Biodegradation of PAHs in soil: Influence of chemical structure, concentration and multiple amendment. Environ. Pollut. 158, 3411-3420.

Cox, L., Cecchi, A., Celis, R., Hermosin, M., Koskinen, W., Cornejo, J., 2001. Effect of exogenous carbon on movement of simazine and 2, 4-D in soils. Soil Sci. Soc. Am. J. 65, 1688-1695.

Eaton, R.W., Chapman, P.J., 1992. Bacterial metabolism of naphthalene: construction and use of recombinant bacteria to study ring cleavage of 1, 2-dihydroxynaphthalene and subsequent reactions. J. Bacteriol. 174, 7542-7554.

Farber, S., Griner, B., 2000. Valuing watershed quality improvements using conjoint analysis. Ecol. Econ. 34, 63-76.

Gan, C., 1992. A conjoint analysis of wetland-based recreation: a case study of Louisiana waterfowl hunting. PhD Thesis. Louisiana State University.

Green, P., Srinivasan, V., 1990. Conjoint analysis in marketing: new developments with implications for research and practice. J. Marketing 54, 3-19.

Gregory, R., Lichtenstein, S., Slovic, P., 1993. Valuing environmental resources: a constructive approach. J. Risk Uncertainty 7, 177-197.

Hair, J., Black, B., Babin, B., Anderson, R., & Tatham, R. , 2006. Multivariate data analysis (6th ed.). Upper Saddle River, NJ: Prentice Hall.

Johnson, F., Desvousges, W., 1997. Estimating stated preferences with rated-pair data: environmental, health, and employment effects of energy programs. J. Environ. Econ. Manag. 34, 79-99.

Kördel, W., Bernhardt, C., Derz, K., Hund-Rinke, K., Harmsen, J., Peijnenburg, W., Comans, R., Terytze, K., 2013. Incorporating availability/bioavailability in risk assessment and decision making of polluted sites, using Germany as an example. J. Hazard. Mater., http://dx.doi.org/10.1016/j.jhazmat.2013.1005.1017.

Lareau, T., Rae, D., 1989. Valuing WTP for diesel odor reductions: an application of contingent ranking technique. Southern Econ. J. 55, 728-742.

Latawiec, A.E., Swindell, A.L., Simmons, P., Reid, B.J., 2011. Bringing Bioavailability into Contaminated Land Decision Making: The Way Forward? Crit. Rev. Env. Sci. Tec 41, 52-77.

Lohrke, F.T., Holloway, B.B., Woolley, T.W., 2010. Conjoint Analysis in Entrepreneurship Research A Review and Research Agenda. Organ. Res. Meth. 13, 16-30.

Lord, R.A., Atkinson, J., Scurlock, J.M.O., Lane, A.N., Rahman, P.K.S.M., Connolly, H.E., Street, G., 2007. Biomass, Remediation, re-Generation (BioReGen Life Project): Reusing brownfield sites for renewable energy crops. In: Proceedings 15th European Biomass Conference & Exhibition, 7-11 May 2007, Milan.

Mackenzie, J., Eduljee, B.R., 1990. Conjoint-analysis of demand for waterfowl hunting. Am. J. Agr. Econ. 72, 1360-1360.

Madurantakam, P.A., Rodriguez, I.A., Cost, C.P., Viswanathan, R., Simpson, D.G., Beckman, M.J., Moon, P.C., Bowlin, G.L., 2009. Multiple factor interactions in biomimetic mineralization of electrospun scaffolds. Biomaterials. 30, 5456-5464.

McCoullough, D., 2002. A user's guide to conjoint analysis: before starting out you need to know where the landmines are. Market Res. 14, 18-23.

Muramatsu, R., Nakamura, Y., 2002. Evaluation of lighting environment using conjoint analysis (Part 1) - For the case of office. J. Light Visual Environ. 26, 30-39.

Namkoong, W., Hwang, E.Y., Park, J.S., Choi, J.Y., 2002. Bioremediation of diesel-contaminated soil with composting. Environ. Pollut. 119, 23-31.

Opaluch, J., Swallow, S., Weaver, T., Wessells, C., Wichelns, D., 1993. Evaluating impacts from noxious facilities: including public preferences in current siting mechanisms. J. Environ. Econ. Manag. 24, 41-59.

Ortega-Calvo, J., Tejeda-Agredano, M., Jimenez-Sanchez, C., Congiu, E., Sungthong, R., Niqui-Arroyo, J., Cantos, M., 2013. Is it possible to increase bioavailability but not environmental risk of PAHs in bioremediation? J. Hazard. Mater., http://dx.doi.org/10.1016/j.jhazmat.2013.1003.1042.

Peace, G.S., 1993. Taguchi methods: a hands-on approach. Addison-Wesley Reading, MA.

Puglisi, E., Cappa, F., Fragoulis, G., Trevisan, M., Del Re, A.A.M., 2007. Bioavailability and degradation of phenanthrene in compost amended soils. Chemosphere 67, 548-556.

Reid, B.J., Fermor, T.R., Semple, K.T., 2002. Induction of PAH-catabolism in mushroom compost and its use in the biodegradation of soil associated phenanthrene. Environ. Pollut. 118, 65-73.

Reid, B.J., Jones, K.C., Semple, K.T., 2000. Bioavailability of persistent organic pollutants in soils and sediments-a perspective on mechanisms, consequences and assessment. Environ. Pollut. 108, 103-112.

Roe, B., Boyle, K., Teisl, M., 1996. Using Conjoint Analysis to Derive Estimates of Compensating Variation. J. Environ. Econ. Manag. 31, 145-159.

Sandrin, T.R., Maier, R.M., 2003. Impact of metals on the biodegradation of organic pollutants. Environ. Health Persp. 111, 1093-1101.

Sayara, T., Sarrà, M., Sánchez, A., 2010. Effects of compost stability and contaminant concentration on the bioremediation of PAHs-contaminated soil through composting. J. Hazard. Mater. 179, 999-1006.

Semple, K.T., Morriss, A.W.J., Paton, G.I., 2003. Bioavailability of hydrophobic organic contaminants in soils: fundamental concepts and techniques for analysis. Eur. J. Soil Sci. 54, 809-818.

Semple, K.T., Reid, B.J., Fermor, T.R., 2001. Impact of composting strategies on the treatment of soils contaminated with organic pollutants. Environ. Pollut. 112, 269-283.

SEPA, 2011. Paragraph 9 Exemption for "The reclamation or improvement of land", Scottish Environment Protection Agency. www.sepa.org.uk.

Stuart, B., Bowlen, G., Kosson, D., 1991. Competivive sorption of benzene, toluene and the xylenes onto soil. Environ. Prog. 10, 104-109.

Thomas, J.M., Ward, C.H., Raymond, R.L., Wilson, J.T., Loehr, R.C. (Eds.), 1992. Bioremediation. Encyclopedia of Microbiology. Academic Press, San Diego, California.

White, J.C., Hunter, M., Pignatello, J.J., Alexander, M., 1999. Increase in bioavailability of aged phenanthrene in soils by competitive displacement with pyrene. Environ. Toxicol. Chem. 18, 1728-1732.

Wu, G., Kechavarzi, C., Li, X., Sui, H., Pollard, S.J.T., Coulon, F., 2013a. Influence of mature compost amendment on total and bioavailable polycyclic aromatic hydrocarbons in contaminated soils. Chemosphere 90, 2240-2246.

Wu, G., Kechavarzi, C., Li, X., Wu, S., Pollard, S.J., Sui, H., Coulon, F., 2013b. Machine learning models for predicting PAHs bioavailability in compost amended soils. Chem. Eng. J. 223, 747-754.

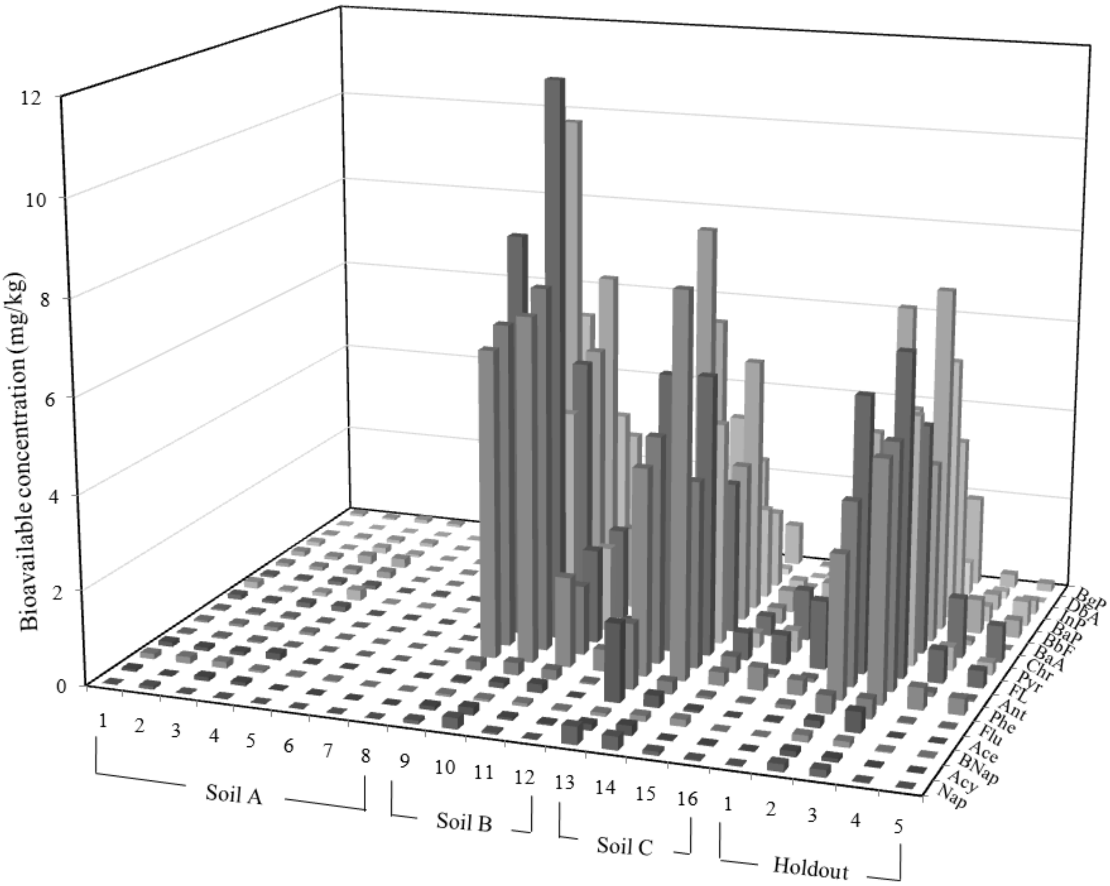


Fig. 1 Distribution of bioavailable concentration of 16 PAHs in the 16 orthogonal designed profiles and 5 holdout selected profiles

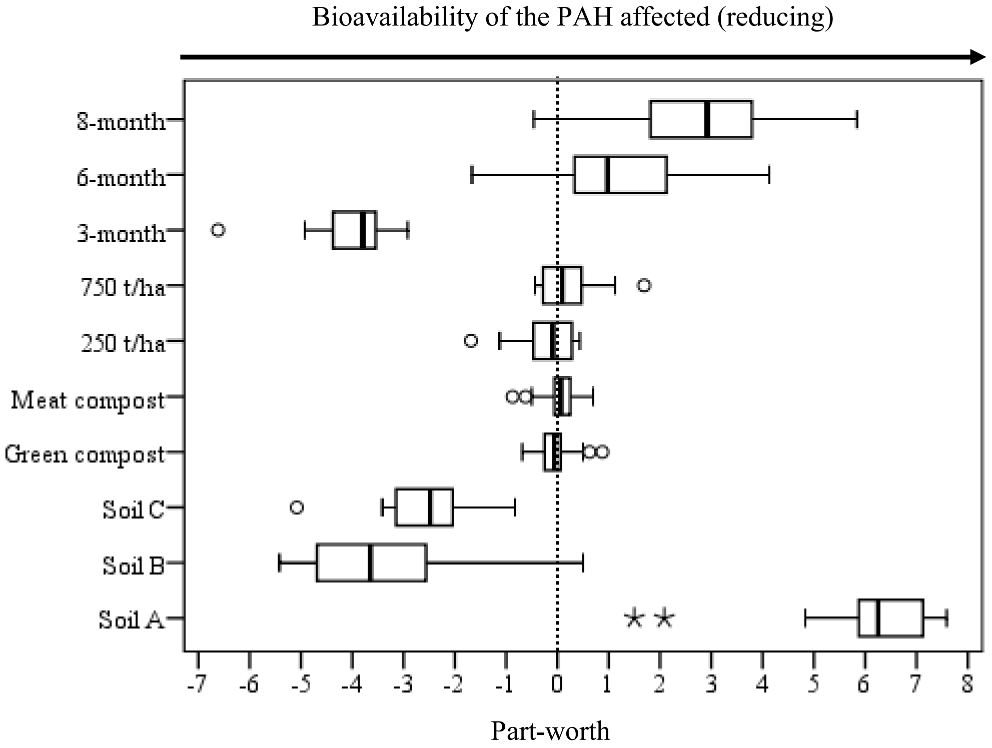


Fig. 2 Boxplot depicting the estimated part-worth values of each level of impact factors. Pearson’s R coefficient: 0.994 (p < 0.001); Kendall’s tau coefficient: 0.867 (p < 0.001). The central rectangle spans the first quartile to the third quartile (the interquartile range, IQR). A segment inside the rectangle shows the median and the "whiskers" on the right and left of the box show the locations of the minimum and maximum. The circles and pentacles represent the outliers (≥3 times of IQR on the right of the third quartile or ≥3 times of IQR on the left of the first quartile) and suspected outliers (≥1.5 times of IQR on the right of the third quartile or ≥1.5 times of IQR on the left the first quartile), respectively.

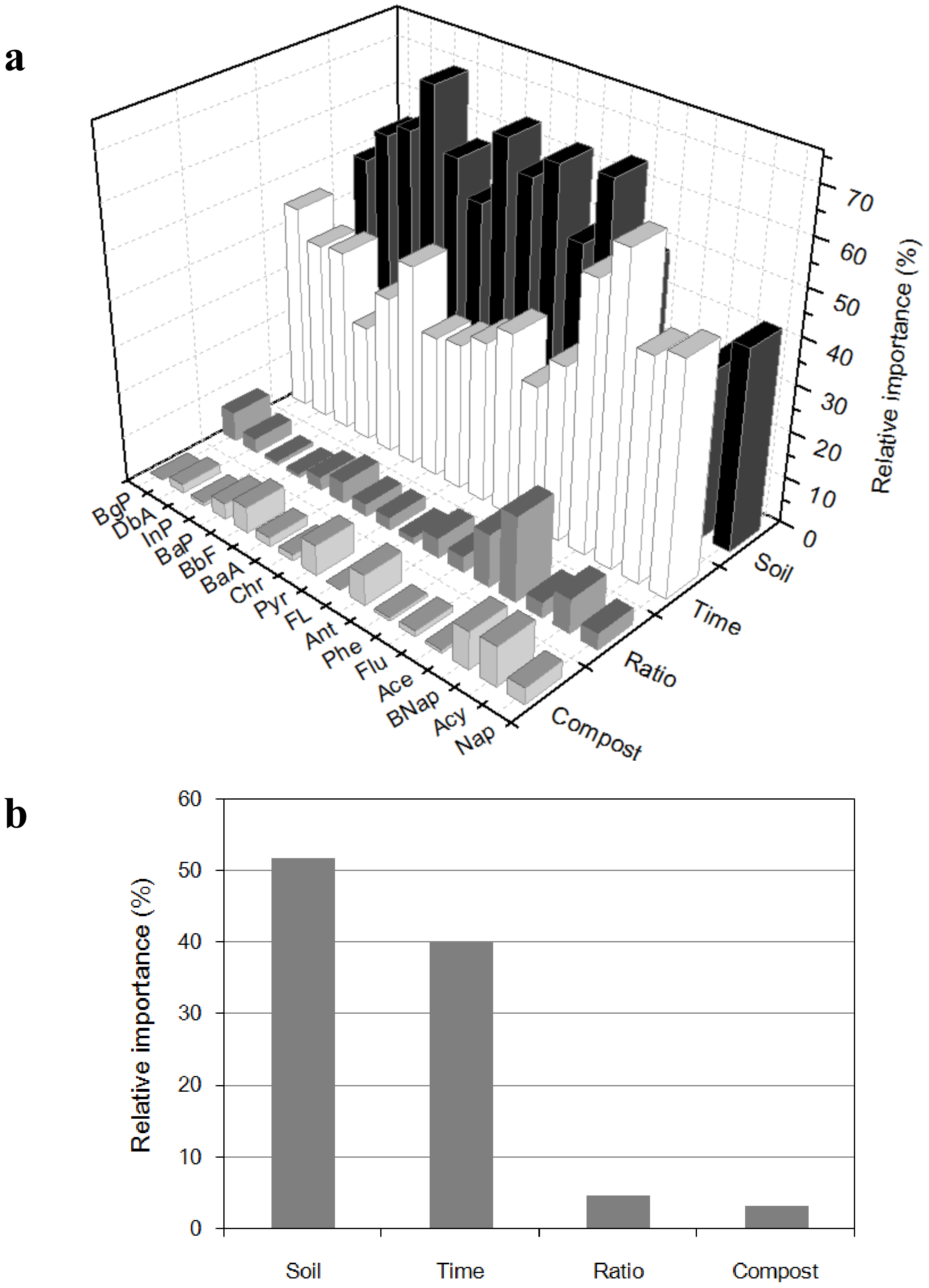


Fig. 3 Relative importance of soil, compost, ratio of compost to soil, and time on the bioavailability of (a) individual PAHs and (b) overall samples (n=16)

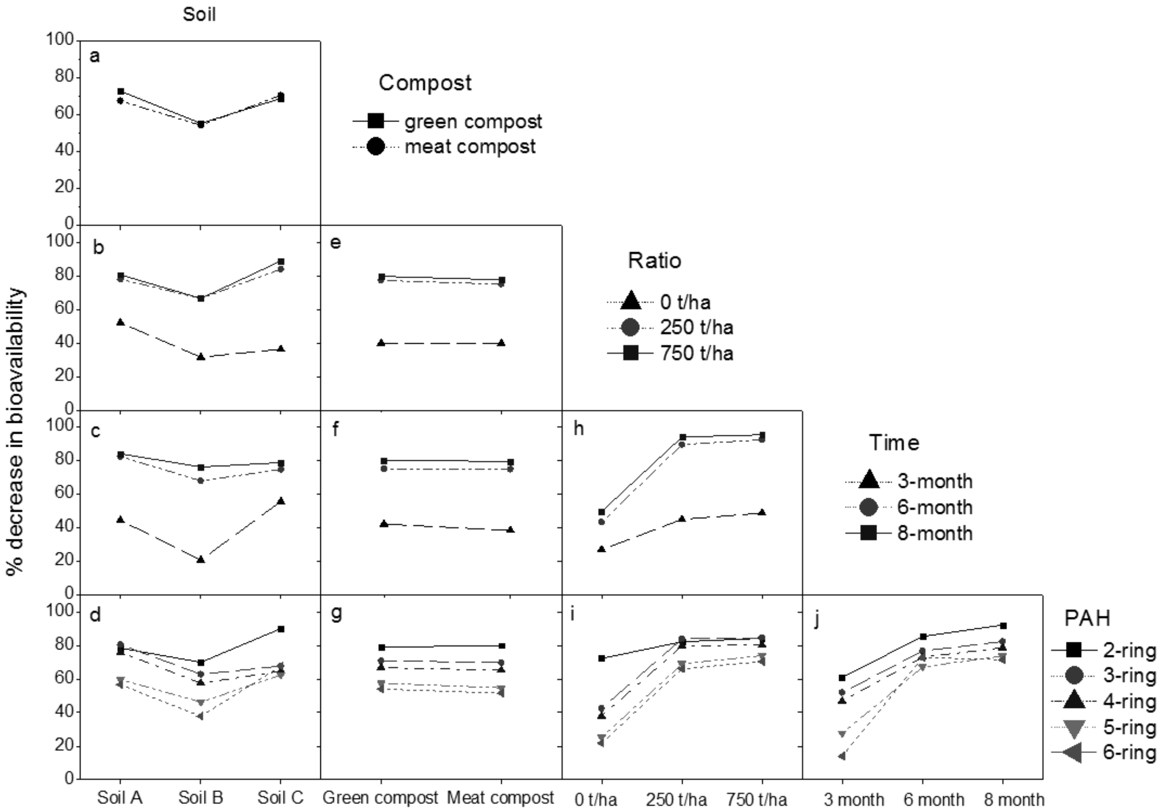
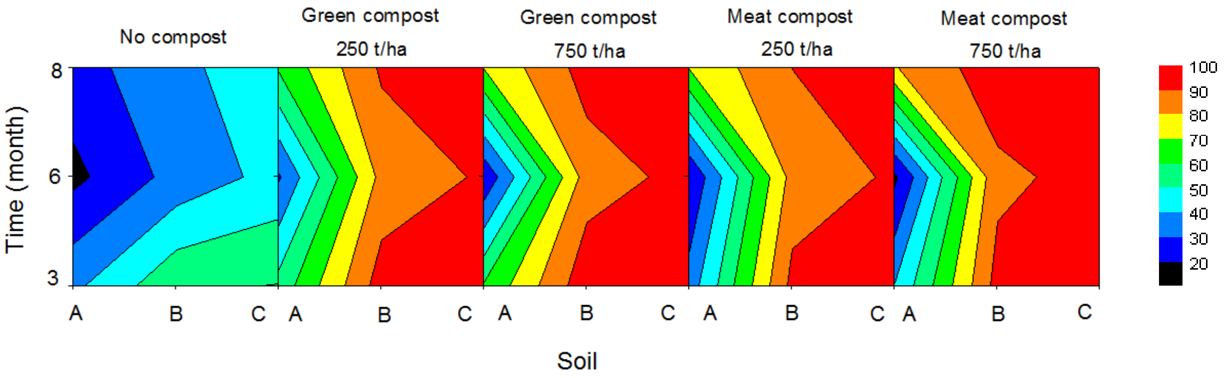
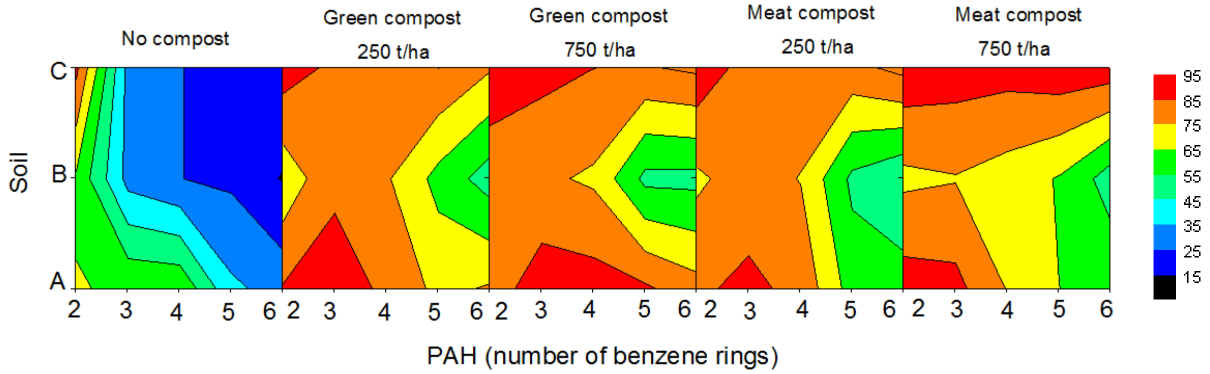


Fig. 4 Two-factor interaction plot matrix demonstrating the presence and strength of interactions on bioavailability decrease. The five factors are listed along the diagonal and the ten possible two-factor interactions are plotted at the intersection of the corresponding factors. Interaction is present if the slopes of the lines are not parallel. The greater the deviation from parallelism, the greater the strength of interaction is.

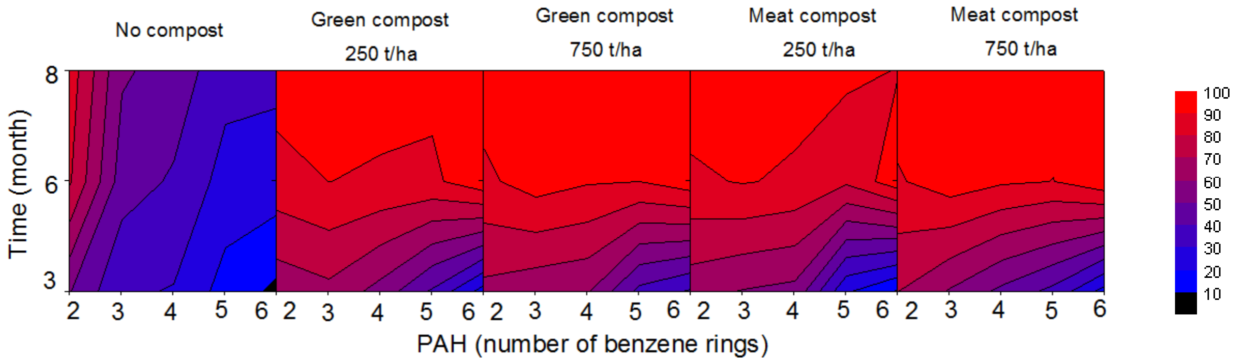
(a)T×S×C×R



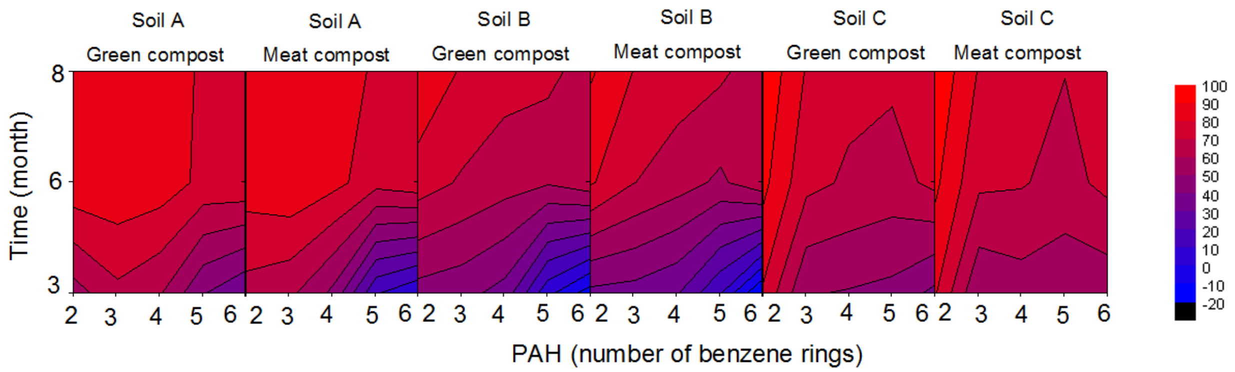
(b) S×P×C×R



(c)T×P×C×R

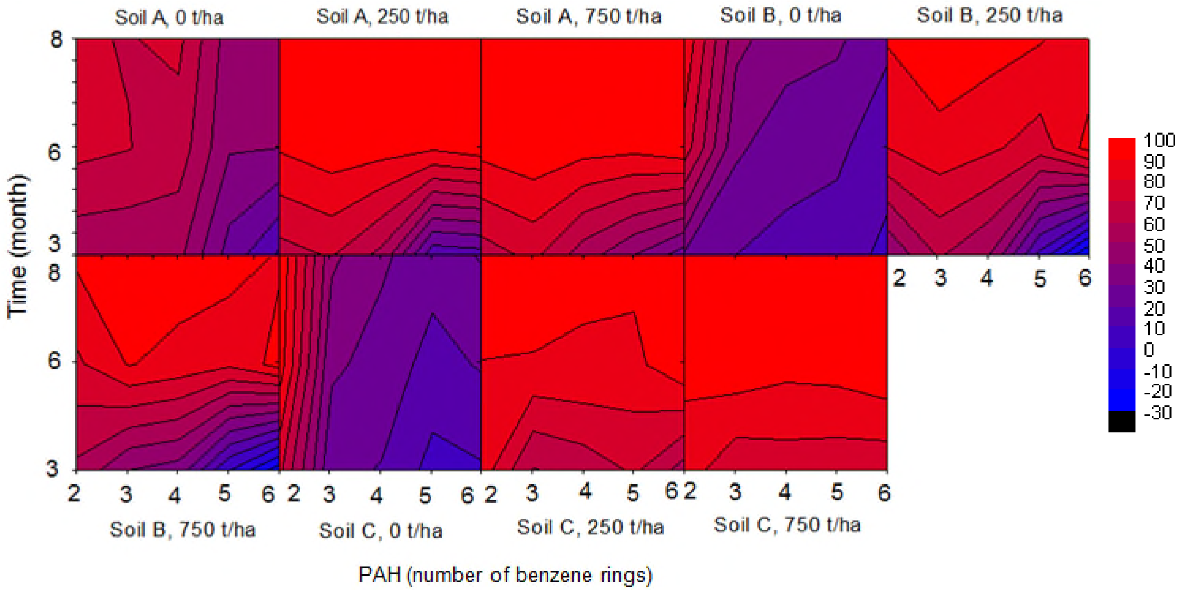


(d)T×P×S×C



(e)T×P×S×R

517



Soil A, 0 t/ha
Soil A, 250 t/ha
Soil A, 750 t/ha
Soil B, 0 t/ha
Soil B, 250 t/ha
Soil B, 750 t/ha
Soil C, 0 t/ha
Soil C, 250 t/ha
Soil C, 750 t/ha
Time (month)
8
6
3
2
3
4
5
6
PAH (number of benzene rings)
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30

518

519

Table 1 Orthogonal design and holdout profiles in the conjoint analysis

		Profiles	Compost	Ratio (t/ha)	Time (month)
Orthogonal profiles	Soil A	1	Green	250	3
		2	Green	750	3
		3	Meat	250	3
		4	Meat	750	3
		5	Green	250	6
		6	Meat	750	6
		7	Green	750	8
		8	Meat	250	8
	Soil B	9	Green	750	3
		10	Meat	750	3
		11	Green	250	6
		12	Meat	250	8
	Soil C	13	Green	250	3
		14	Meat	250	3
		15	Meat	750	6
		16	Green	750	8
Holdout profiles	Soil C	1	Meat	250	8
	Soil B	2	Green	250	3
	Soil B	3	Meat	250	3
	Soil B	4	Green	250	8
	Soil B	5	Meat	750	8

Table 2 Estimated main effects and multiple factor interactions using ANOVA by Tukey test

Source	df	F	MS	p	Source	df	F	MS	p
T	2	1233	83671	0.000	T×S×C	4	6	431	0.000
S	2	202	13707	0.000	T×S×R	8	13	911	0.000
C	1	4	283	0.042	T×S×P	16	7	457	0.000
R	2	1247	84630	0.000	T×C×R	4	0.8	55	0.520
P	4	186	12657	0.000	T×C×P	8	0.3	19	0.971
T×S	4	71	4822	0.000	T×R×P	16	13	877	0.000
T×C	2	3	198	0.056	S×C×R	4	2	166	0.047
T×R	4	69	4713	0.000	S×C×P	8	2	156	0.021
T×P	8	33	2276	0.000	S×R×P	16	11	765	0.000
S×C	2	8	577	0.000	C×R×P	8	0.9	60	0.527
S×R	4	41	2796	0.000	T×S×C×R	8	2	112	0.108
S×P	8	19	1324	0.000	T×S×C×P	16	3	189	0.000
C×R	2	1	72	0.348	T×S×R×P	32	4	308	0.000
C×P	4	0.9	60	0.474	T×P×C×R	16	0.5	36	0.928
R×P	8	40	2739	0.000	S×C×R×P	16	1.8	124	0.028

MS: mean of squares; df: degree of freedom

Supplementary Materials

Influence and interactions of multi-factors on the bioavailability of PAHs in compost amended contaminated soils

Guozhong Wu [a,b,c], Xingang Li [a,d], Cédric Kechavarzi [b], Ruben Sakrabani [b], Hong Sui [a,d], Frédéric Coulon [b,e] *

[a] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

[b] Department of Environmental Science and Technology, Cranfield University, Cranfield MK43 0AL, UK

[c] Division of Ocean Science and Technology, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

[d] National Engineering Research Centre for Distillation Technology, Tianjin 300072, China

[e] Centre for Research in Environmental, Coastal and Hydrological Engineering, School of Civil Engineering, Surveying and Construction, University of KwaZulu-Natal, Howard College Campus, Durban, 4041, South Africa

* Corresponding author:

E-mail: f.coulon@cranfield.ac.uk

Phone: +44 1234 754 981

Fax: +44 1234 751 036

Number of tables: 1

Number of figures: 3

Table SM-1 Rankings of the 16 orthogonal profiles tested for each PAH. The top row indicates the profiles with the largest bioavailability while the last row indicated the smallest one.

Ranking	Nap	Acy	BNap	Ace	Flu	Phe	Ant	FL	Pyr	Chr	BaA	BbF	BaP	InP	DbA	BgP
1	13	14	15	13	13	14	10	10	9	9	13	9	9	13	9	13
2	14	10	2	14	14	10	9	9	13	10	10	10	10	9	10	10
3	10	13	3	11	10	9	13	14	14	14	9	13	14	10	12	9
4	15	3	14	4	11	13	14	13	10	13	14	14	11	14	13	14
5	9	9	1	10	9	11	11	11	11	11	11	11	13	12	14	12
6	2	4	13	1	15	16	15	16	16	16	15	15	12	16	16	16
7	11	11	11	3	3	12	16	15	12	12	16	12	16	11	1	3
8	16	1	10	2	12	15	3	12	15	15	4	16	15	4	4	11
9	4	12	9	15	2	3	2	4	4	4	3	4	3	3	11	1
10	3	16	4	9	16	4	1	3	1	3	2	3	1	2	15	4
11	1	15	12	5	1	2	12	1	3	1	1	1	4	15	2	2
12	12	2	6	8	4	1	4	2	2	2	12	2	2	1	3	15
13	5	6	5	6	5	5	5	5	6	6	6	6	7	7	7	8
14	8	7	16	16	6	6	7	6	5	5	5	5	6	5	8	7
15	7	5	7	12	8	8	6	8	8	8	8	8	5	8	5	6
16	6	8	8	7	7	7	8	7	7	7	7	7	8	6	6	5

a

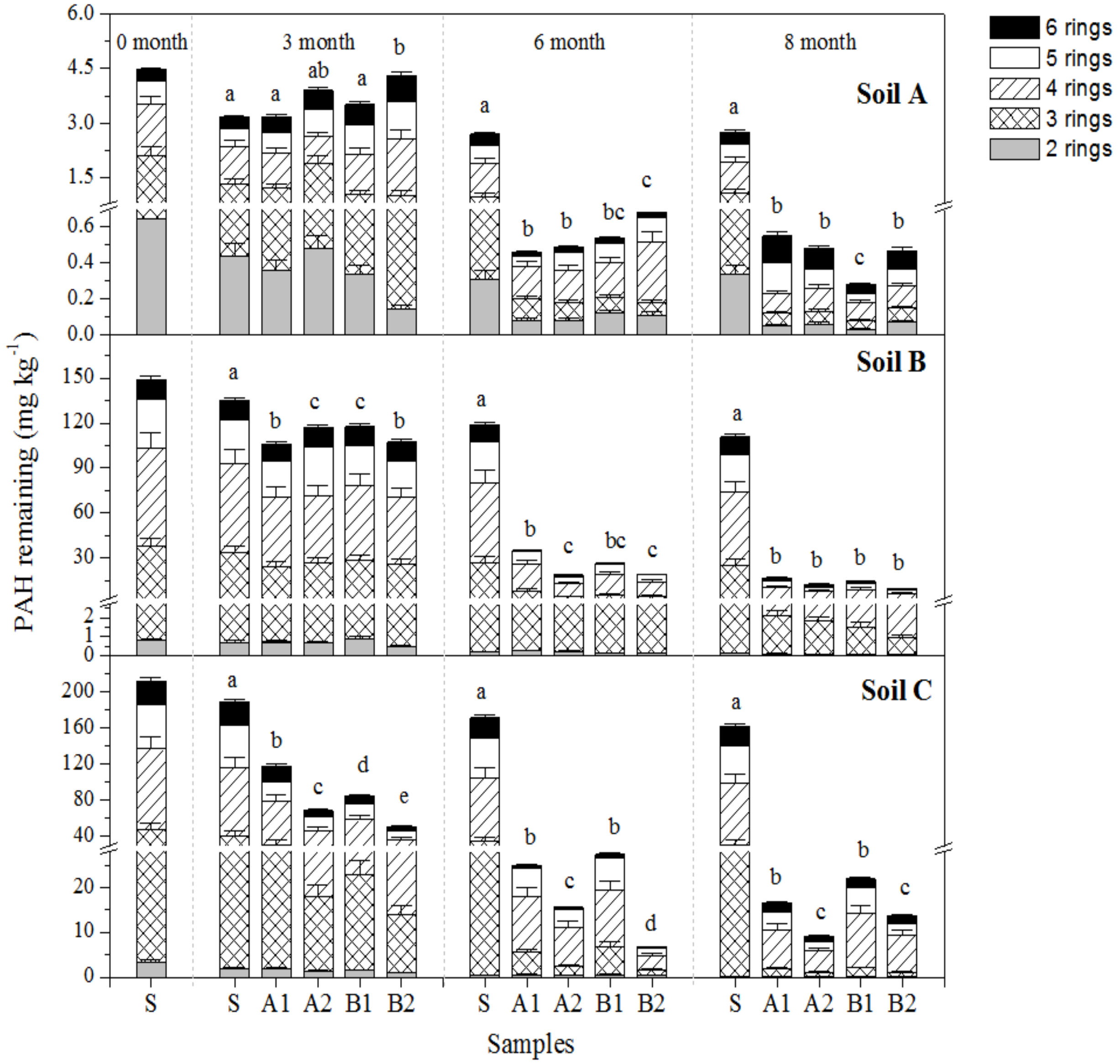


Fig. SM-1 Total concentration of PAHs in the blank soil (S) and the soil amended with A1 (Green compost, 250 t ha^{-1}), A2 (Green compost, 750 t ha^{-1}), B1 (Meat compost, 250 t ha^{-1}) and B2 (Meat compost, 750 t ha^{-1}) after incubation for 0, 3, 6 and 8 months. Adapted from Wu et al., 2013.

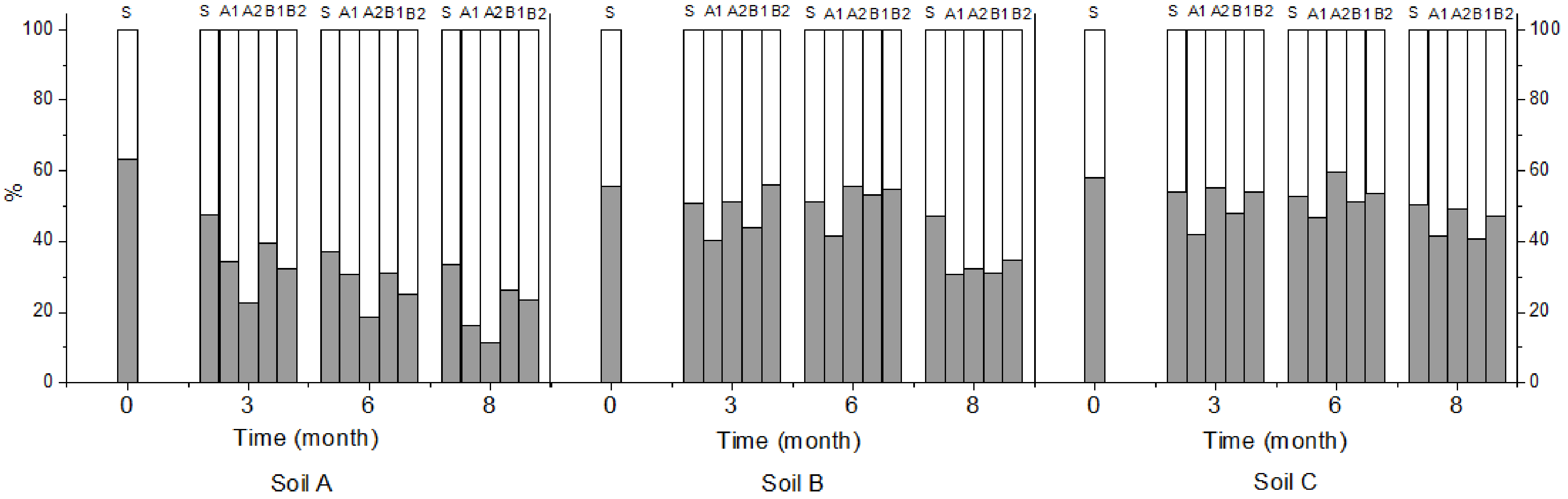


Fig. SM-2 Percentage of bioavailable (■) and sorbed (□) fractions in the total concentration of Σ_{16}PAHs in the blank soil (S) and in the soil amended with A1 (Green compost, 250 t ha^{-1}), A2 (Green compost, 750 t ha^{-1}), B1 (Meat compost, 250 t ha^{-1}) and B2 (Meat compost, 750 t ha^{-1}). Adapted from Wu et al., 2013.

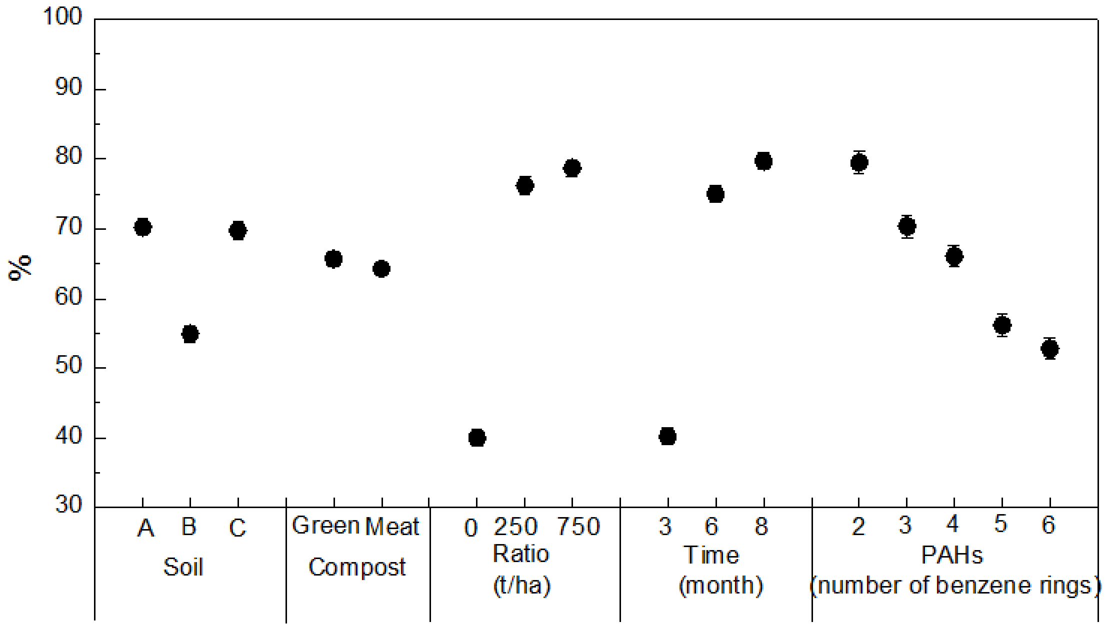


Fig. SM-3 Sensitivity analysis of the factors on the percentage loss of bioavailable PAHs

Reference:

G. Wu, C. Kechavarzi, X. Li, H. Sui, S.J.T. Pollard, F. Coulon, Influence of mature compost amendment on total and bioavailable polycyclic aromatic hydrocarbons in contaminated soils, Chemosphere 90 (2013) 2240-2246.