



Oxidation of anthracene using waste Mn oxide minerals: The importance of wetting and drying sequences

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ABSTRACT

PAHs are a common problem in contaminated urban soils due to their recalcitrance. This study presents results on the oxidation of anthracene on synthetic and natural Mn oxide surfaces. Evaporation of anthracene spiked Mn oxide slurries in air results in the oxidation of 30% of the anthracene to anthraquinone. Control minerals, quartz and calcite, also oxidised a small but significant proportion of the anthracene (4.5% and 14% conversion, respectively) when spiked mineral slurries were evaporated in air. However, only Mn oxide minerals showed significant anthracene oxidation (5–10%) when evaporation took place in the absence of oxygen (N₂ atmosphere). In the fully hydrated systems where no drying took place, natural Mn oxides showed an increase in anthracene oxidation with decreasing pH, with a conversion of 75% anthracene at pH 4. These results show both acidification and drying favor the oxidation of anthracene on Mn oxide mineral surfaces. It has also been demonstrated that non-redox active mineral surfaces, such as calcite, may play a role in contaminant breakdown during wetting and drying sequences. Given that climate changes suggest that wetting and drying sequences are likely to become more significant these results have important implications for contaminated land remediation technologies.

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1. Introduction

Land is a valuable but uniquely finite resource. Contaminated land is an international problem and it is high on the agenda of environmental and regeneration problems in much of Europe and North America. Persistent organic pollutants (POPs) such as polycyclic-aromatic hydrocarbons (PAH) are one of the main causes of concern particularly when present in ‘cocktail’ sites where there are mixtures of metals and POPs. The introduction of the EU Land-fill Directive in 2006 has resulted in a move away from dig and dump as a remediation strategy in Europe and there is increasing interest in the development of new cost-effective *in situ* methods to remediate brownfield sites.

Manganese oxides are one of the most powerful oxidizing agents found in soils, and there are numerous studies demonstrating their capacity to breakdown POPs of various chemistries as well as immobilize metal ions [1,16]. For this reason Mn oxides are considered a beneficial component of soil's defense against contamination. Addition of Mn oxides to soil as a remediation strategy is appealing due to the ‘slow release’ nature of the oxidizing capac-

ity in contrast to stronger more expensive and less sustainable oxidation agents, such as Fenton reagents, which are short lived in soils, often being scavenged by natural organic matter before the target compounds have been reached [2]. Although cheap sources of Mn oxides are uncommon, certain waste products such as the mine tailings produced in the South African Mn mining operations as well as Mn containing water treatment residuals from the clean water treatment industry in temperate climates are possible sources of uncontaminated natural Mn oxides which may be suitable for land remediation.

Anthracene is a three-ringed PAH which is listed as a priority contaminant by the U.S.E.P.A. It is often viewed as a model PAH because of its low water solubility and the fact that it has the same arrangement of fused aromatic rings as the more complex PAHs [3]. There are very few reports of abiotic interactions between PAHs and soil minerals under oxic conditions. Pyrene degradation has been observed when the Mn oxide birnessite was gently ground with PAH contaminated soil [4]. Other reports of abiotic interactions between Mn oxides and PAHs have not shown any positive reaction [5]. It has been demonstrated that anthracene can be oxidised to anthraquinone via Mn (III) peroxidase mediated reactions [6]. The hydroxylation of anthracene is thought to occur by radical formation followed by nucleophilic attack of water molecules. The hydroxyl groups are then further oxidised to quinone moieties [7]. Kopinke and Remmler [8] report that Mn and Fe oxides are capable

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of catalysing free radical formation and polymerisation reactions of PAHs during the thermal treatment of contaminated sediment. In pure mineral studies, Remmler and Kopinke [9] established that acid activated clays had the highest conversion rates of PAHs and that acid activation plays a more important role in the polymerising capacity of a surface than high surface area.

One of the main hindrances in the abiotic and biotic degradation of PAHs is the low water solubility of the compounds which in the case of mineral interaction, prevents intimate contact between the pollutant and the mineral surface [4]. One factor which influences pollutant–mineral contact is wetting and drying sequences. Sorption of hydrophobic organic compound vapours onto mineral surfaces is highly dependent on surface moisture content [10], which is considered to be largely due to the displacement of sorbed organic compounds by water molecules. Sorption of organic molecules to clay and oxide minerals is greatest when the moisture content is below one monolayer of water coverage, but there is still an exponential decrease in sorption up until 10 water monolayers [10]. This would suggest that mineral surfaces may still impart an influence even while significantly hydrated. However few authors have used drying as a method for achieving contact between hydrophobic organic contaminants and mineral surfaces despite it being representative of natural conditions in the unsaturated zone. It should be noted that it is extremely difficult to measure Eh and pH at a drying mineral surface and also that a drying system is not in thermodynamic equilibrium. For these reasons we have not presented either stoichiometric or thermodynamic data.

Evaporation of water from a mineral surface can also have a chemical effect. Drying the mineral–water interface has been shown to be an acidifying process [11], which may affect oxidative interactions between minerals and organic molecules. Both the increased sorption and changing chemical environment on drying mineral interfaces, suggests that contaminant behaviour in dried systems may be different to behaviour in hydrated systems. The aim of this investigation is to determine the potential of Mn oxides, both synthetic and those present in a mining waste, to oxidise the PAH anthracene in both fully hydrated as well as air-dried systems. Since wetting and drying sequences are predicted to become more pronounced by climate change models [12] this work has important implications for contaminated land remediation technologies which are applied to the unsaturated zone.

2. Materials and methods

Natural Mn oxide minerals were collected from tailings materials of the Kalahari manganese mines in the Northern Cape Province of South Africa. The detailed chemical and physical properties of these Mn oxide tailings (Mn tailings) are presented in Clarke et al. [13]. The BET-N₂ specific surface areas of the Mn tailings and other pure minerals used in this work are as follows (m²/g): Mn tailings (2.40); quartz (0.84); calcite (1.00) and synthetic Mn₂O₃ (0.65).

The Mn tailings, calcite (CC) (Derbyshire limestone; TRUCAL, Tarmac), quartz (Tarmac) and synthetic Mn₂O₃ (MO) (Sigma–Aldrich) were reacted with anthracene (AC). Originally quartz and calcite were intended to serve as real mineral controls but it was observed that these mineral phases were reactive during drying reactions and thus could not be used as controls but have been included in the results. Unless specified all samples were prepared in triplicate.

2.1. Drying experiments

The pH was not amended in the drying experiments. Samples were spiked with anthracene using a minimal solvent, single step rehydration/spiking procedure [14]. Briefly, 0.4 mL DI was added to acid washed amber vials. A 7 μ L aliquot of anthracene stock solution

(4 g L⁻¹) was added to the water, and 1 g of mineral sample immediately stirred in with a glass spatula to make a moist crumbly paste (containing a total of 2.26 mg of anthracene). Half the samples were sealed using Teflon lined caps and half the samples were lightly covered in foil to omit light while allowing slow air-drying. The samples were placed in a fume cupboard at 28 °C for 7 days before extraction. The above procedure was repeated under a nitrogen purge. On a separate set of Mn tailings samples the mineral–water slurries were air-dried to varying degrees in order to monitor the chemical reactions at various moisture contents.

To determine if the oxidation reactions are influenced by the type of evaporating solvent, the drying experiments were repeated with the Mn tailings and calcite, replacing the water with cyclohexane (i.e. evaporation of a spiked cyclohexane–mineral slurry). To ensure that all the moisture was removed before the evaporation of cyclohexane, the samples were oven-dried (104 °C) prior to the reaction. In half the samples the cyclohexane was allowed to evaporate while an identical set were sealed to prevent evaporation. Mixing of the latter samples was achieved by placing them on a reciprocal shaker, set at 250 rpm for the 7 day period.

2.2. pH experiments

The pH experiments were conducted in a series of 0.2 M acetate buffers prepared at pH 3, 4, 5 and 6. The Mn tailings and quartz (1 g) were weighed into acid washed amber bottles and 20 mL of the acetate buffer solutions added. These suspensions were shaken for 30 min before the pH of the supernatants were measured. The pH values in the quartz samples were within 0.05 units of the original pH while pH in the tailings treatment showed a slight drift, especially in the pH 6 buffer, which is on the margin of the acetate buffering range. Although the use of acetate to buffer reactions at pH 6 may be questionable, it was decided that it would be better to treat all samples with the same organic buffer to avoid differences in anthracene solubility. The data was plotted according to the final pH of the suspension. Samples were spiked with a 10 μ L aliquot of anthracene stock, sealed with Teflon caps and shaken on a reciprocal shaker (250 rpm) for 5 days. Cyclohexane was added to the spiked acetate–mineral slurries and extracted using the sonication–shaking procedure described below.

2.3. Extraction procedures

Extraction of anthracene (AC) and the oxidation product, anthraquinone (AQ), was achieved using a simple sonication method. The anthracene extraction efficiency using this technique was >89% for hydrated samples. Since extraction of hydrophobic compounds from dried soils using non-polar extractants is inefficient [15] a range of extraction solvents (cyclohexane, cyclohexane plus water, methanol and acetonitrile) were tested. The cyclohexane plus water extraction procedure described below, gave optimal recovery for both anthracene and anthraquinone and was used for all the experiments.

Both dry and moist samples were extracted in the same fashion. A volume of 10 mL water was added to the spiked samples followed by 10 mL cyclohexane. The samples were sealed with Teflon lined caps and placed in a sonic bath for 2 h. The samples were then shaken on a reciprocal shaker set at 250 rpm for 24 h. Cyclohexane was separated from the water and solid phases using Fisherbrand phase separation paper. Filtered extracts were collected in amber vials for UV and HPLC analysis.

3. Results and discussion

The mineralogical, chemical and physical properties of the tailings have been presented elsewhere [13]. Briefly, the tailings are

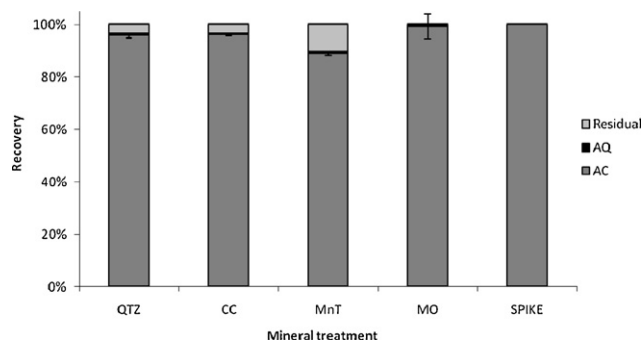


Fig. 1. Percentage recovery (mole based) of anthracene (AC) and anthraquinone (AQ) in extracts from hydrated experiments (no evaporation) quartz (QTZ), calcite (CC), Mn tailings (MnT), and purchased Mn_2O_3 (MO) samples spiked with anthracene. No adjustment to pH was made in these experiments.

a by-product of Mn ore extraction in the Kalahari Mn fields. They contain high proportions of Mn oxides (up to 33%) with accessory carbonate and silicate minerals. The net oxidation state of Mn in the tailings is 3+ with manganite being the dominant Mn oxide mineral phase. The tailings are net alkaline with a pH of 8.8 measured in water. The point of zero charge of the tailings was determined to be below pH 4.

3.1. The effect of surface drying on anthracene oxidation

The concentration of anthracene (calculated as % of the original anthracene spike measured after addition to the glass vials) measured after contact with minerals under hydrated conditions (no drying) for 7 days is given in Fig. 1. No adjustment to pH was made.

Anthracene recovery from the hydrated samples was good for all treatments (>89%) (Fig. 1). The residual was calculated as follows: $100 - [AQ + AC]$ and can be used to determine the recovery of organic compounds. Certain samples (MO) showed 99% recovery thus volatilisation was considered minimal. Trace concentrations (<0.7%) of anthraquinone were detected in the Mn tailings, CC and QTZ treatments. It was observed however that a small degree of mineral drying had occurred around the edges of these vials. No anthracene oxidation was observed in any of the saturated experiments under N_2 (data not shown).

The concentration of anthracene (calculated as % of the original anthracene spike) measured after allowing spiked water slurries to evaporate over 7 days is given in Fig. 2.

Air drying spiked mineral slurries resulted in the oxidation of anthracene to anthraquinone in both the Mn oxide treatments

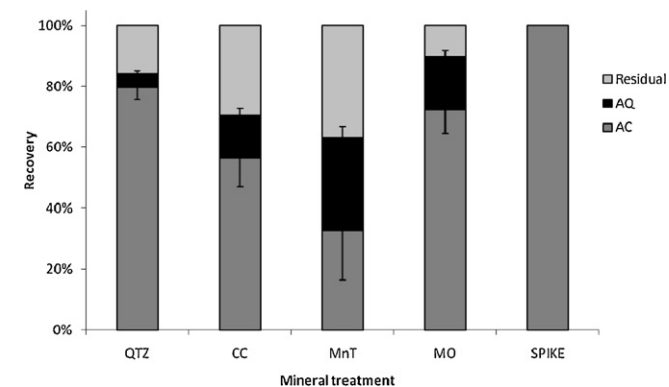


Fig. 2. Percentage recovery (mole based) of anthracene (AC) and anthraquinone (AQ) in extracts from drying experiments quartz (QTZ), calcite (CC), Mn tailings (MnT), and purchased Mn_2O_3 (MO) samples spiked with anthracene. No adjustment to pH was made in these experiments.

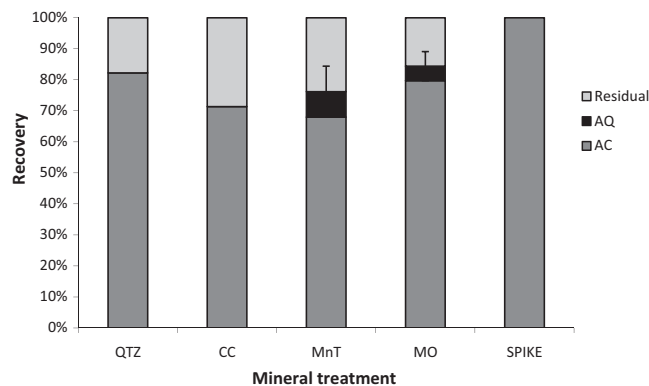


Fig. 3. Percentage recovery (mole based) of anthracene (AC) and anthraquinone (AQ) in extracts from drying experiments (with drying under nitrogen): quartz (QTZ), calcite (CC), Mn tailings (MnT), and purchased Mn_2O_3 (MO) samples spiked with anthracene. No adjustment to pH was made in these experiments.

and the quartz and calcite controls. Air drying also increased the residual component of all mineral treatments. Volatilisation may have contributed to this large residual but it was hard to quantify due to the unexpected oxidative reactions which took place in the original control mineral (quartz and calcite) experiments (see later discussion). A spiked water sample was allowed to evaporate in a clean amber vial in order to quantify any volatilisation loss, however, the evaporation of the moisture resulted in a limited oxidation of anthracene to anthraquinone in quantities similar to those observed in the quartz treatments. Quartz showed the lowest oxidation (4.5%) followed by calcite (14%), MO (17%) and then Mn tailings (30%). The lowest recovery (i.e. largest residual) was also observed in the dried Mn tailings (30%) experiments. To establish the role of oxygen in the oxidation of anthracene on dried mineral surfaces the drying experiments were repeated under nitrogen. Drying under nitrogen produced similar residual values to the experiments in air, however, only the synthetic Mn oxide and the Mn tailings showed anthracene oxidation, with no anthraquinone detected in the calcite or quartz samples (Fig. 3).

The findings from the drying experiments give some unexpected results (see Fig. 2). Anthracene was oxidised to anthraquinone when quartz and calcite were air-dried but no anthraquinone was detected when the spiked slurries were dried under N_2 . This would suggest that oxygen is acting as the oxidant on the drying mineral surface. Why the reaction is enhanced by drying is uncertain but mineral surface characteristics or conformational changes of the anthracene molecule on drying surfaces may make oxidation by oxygen more energetically favourable. The oxidation of anthracene by the Mn oxide treatments under N_2 suggest that the minerals themselves are acting as the oxidant in dried systems.

In order to establish the dependence of anthracene oxidation on moisture content, a series of moist, spiked Mn tailings and quartz samples were dried to different degrees before extraction in cyclohexane. Fig. 4 shows anthracene concentration as a function of gravimetric moisture content for Mn tailings and quartz samples. Anthracene concentration in the quartz treatment decreases slightly as water is evaporated but anthracene loss is substantially larger in the Mn tailings treatment, especially when the water content drops below 5%. This would imply that the oxidation occurs on a drying but not necessarily dry surface.

The acidifying effect of drying mineral surfaces is well known [11]. The acidity is generated by hydrolysis of the last remaining water molecules by exchangeable cations. Any decrease in pH on the Mn oxide mineral surface would increase redox potential of the oxide [16]. To establish if drying-induced acidification plays a role in anthracene oxidation on the mineral surfaces, a

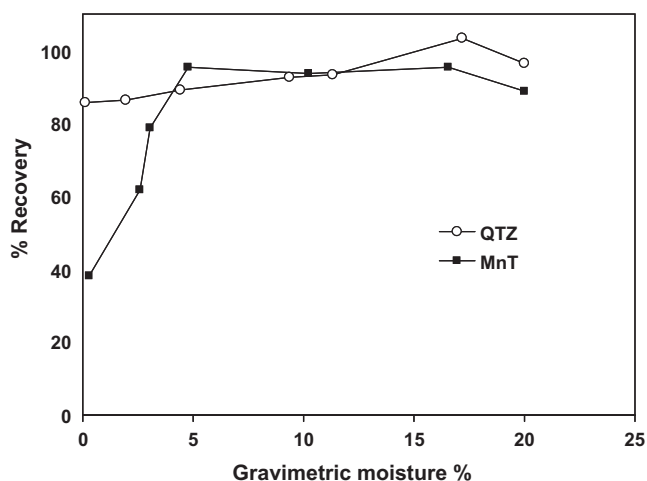


Fig. 4. Anthracene recovery from partially air dried, spiked Mn tailings (MnT) and quartz (QTZ) samples allowed to dry to different degrees.

spiked cyclohexane–mineral slurry was allowed to evaporate. The results (data not shown) show that anthracene is converted to anthraquinone in the Mn tailings and calcite air-dried cyclohexane slurries, in similar proportions to those observed in the water medium. Thus drying induced acidity may not be playing a major role in anthracene oxidation. This suggests that removal of the ‘wetting phase’ (whether a polar or nonpolar solvent) may be necessary for the successful oxidation of anthracene on the mineral surface. One of the changes that would occur during solvent evaporation is enhanced availability of oxygen on the mineral surface. Adsorbed O_2 molecules are seen to be partially responsible for hydroquinone oxidation by clay minerals [17]. The absence of anthraquinone in the calcite and quartz samples dried under N_2 supports the role of O_2 in the oxidation reaction.

In order to determine which mineral surface (per m^2) is the most efficient at oxidising anthracene in air, the amount of anthraquinone produced was normalised by the specific surface area of each mineral. The synthetic manganese oxide, Mn_2O_3 converted the most anthracene to anthraquinone per m^2 of mineral surface (see Fig. 5). Interestingly, calcite was better at converting anthracene to anthraquinone than the Mn tailings. The reasons for this are not clear but may relate to surface properties such as mineral steps present in this specific calcite as previously discussed in [18]. Junta and Hochella [19] discuss the importance of steps as sites of preferential reactivity in sorption reactions but more research would be needed to investigate the role of surface morphology with respect to sorption and oxidation reactions for this particular set of minerals and organic contaminant.

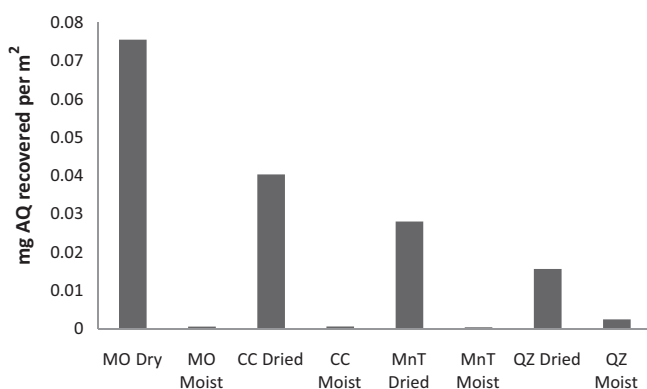


Fig. 5. Anthraquinone recovery (total mg) per m^2 of mineral specific surface area.

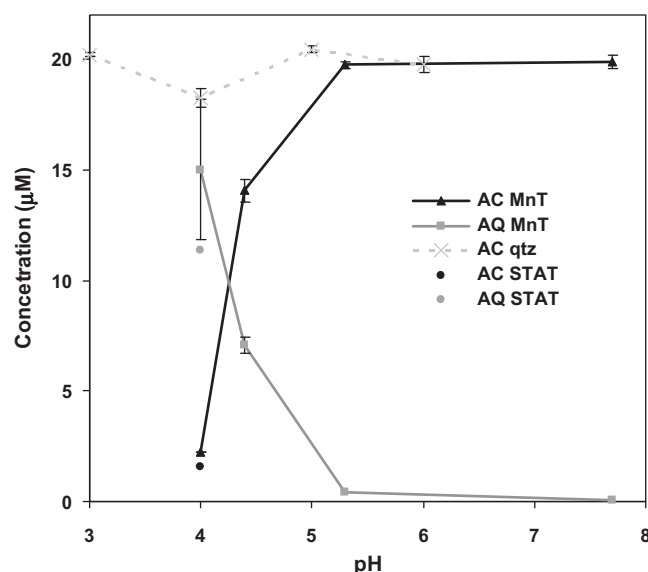


Fig. 6. Anthracene (AC) and anthraquinone (AQ) concentrations after reacting anthracene with the Mn tailings (MnT) and quartz (QTZ) in a series of pH adjusted acetate buffers. Grey and black closed circles represent samples reacted at pH 4 in DI using 0.1 M HCl to control pH. Saturated conditions (no drying).

The above data shows that both manganese oxides and calcite adsorb anthracene under air-dried conditions and that significant oxidation occurs. Attempts to elucidate the transformation reactions on the Mn oxide surfaces were inconclusive but the work under nitrogen suggests that Mn oxides play an additional role in the oxidation reaction (still oxidizing 10% of anthracene to anthraquinone without oxygen cf. 30% with oxygen at gravimetric water contents of <5%).

3.2. The effect of pH on anthracene oxidation

It is well known that Mn oxide mediated oxidation reactions involving polar organic molecules are enhanced at lower pH [16] however it is not clear how pH affects the oxidation of a hydrophobic compound such as anthracene. Anthracene was reacted with the Mn tailings and a quartz control in a series of pH adjusted acetate buffer solutions. The results are shown in Fig. 6.

Decreasing the pH of the bathing solution appears to have an effect on the oxidation of anthracene to anthraquinone, with 75% oxidation occurring at pH 4 in the Mn tailings treatment. The quartz control showed no significant change throughout the pH range.

Tetramethylbenzidine was used to test for the presence of any Mn(III)-acetate complexes [20]. At the buffer concentration used in this experiment (0.2 M) no Mn(III)-complexes were observed, thus it would suggest that the reaction was occurring between the solid phase and anthracene.

The amount of anthracene initially added (2 mg L^{-1}) to the pH treatments far exceeds the aqueous anthracene solubility limit (0.07 mg L^{-1}) yet substantial transformation (75% of total added) to anthraquinone was observed in the pH 4 treatment (Fig. 6). This would suggest that sufficient anthracene mineral contact was obtained in the acetate buffer. Since acetate is likely to increase the solubility of anthracene as is observed with dissolved organic carbon [21], the experiments were repeated in DI using 0.1 M HCl to maintain the pH at 4. The results show substantial conversion (50%) of anthracene to anthraquinone even in the HCl treated solution thus it is clear that appreciable tailings-anthracene contact is also achieved when water is used as the solvent.

Since anthracene is relatively insoluble it is proposed that the conversion of anthracene to anthraquinone results in a

concentration gradient which drives the solid anthracene to dissolve to maintain equilibrium via Le Chatelier's principle. Reaction solutions were continually stirred over the 5 day period which would aid in removal of any formed anthraquinone from the mineral, replenishing reactive surface for further anthracene sorption.

To establish if anthraquinone is broken down further by the tailings under low pH conditions, anthraquinone was also reacted with the Mn tailings in a pH 3.7 acetate buffer. No significant change was observed in the anthraquinone concentration in the Mn tailings or quartz treatments after 5 days reaction time (data not shown). Thus it would appear that anthraquinone is the terminal product of anthracene oxidation by the Mn tailings. The finding that anthraquinone is the terminal product of anthracene oxidation is in agreement with work carried out by other authors using Mn peroxidase in white rot fungi [22].

4. Conclusions

Anthraquinone has been identified as the terminal reaction product in the reaction of anthracene with the Mn oxides under both evaporative and acidic conditions. Anthraquinone is more bioavailable than anthracene and is therefore easier to biodegrade [23]. Hence oxidation of anthracene is considered a beneficial step in PAH degradation. The apparent redox reactivity of non-redox minerals during evaporation of spiked slurries is a surprising finding of this study and is of great relevance to the role of soil minerals in controlling contaminant bioaccessibility. Wetting and drying events are everyday occurrences in many soil environments and are predicted to increase in significance by climate change models [12]. Drying contaminated soil, independent of the presence of redox reactive minerals, may change the speciation of organic compounds but further work is needed to elucidate the mechanism of reactions involved. The importance of the drying process in the oxidation reaction has important implications for the role of minerals such as manganese oxides in land remediation particularly when they are present in the unsaturated zone. Further work is required to determine benefits of adding natural manganese oxide 'waste' minerals to soil as a passive treatment for contaminated land.

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References

- [1] B.M. Tebo, J.R. Bargar, B.G. Clement, G.J. Dick, K.J. Murray, D. Parker, R. Verity, S.M. Webb, Biogenic Mn oxides: properties and mechanisms of formation, *Annu. Rev. Earth Planet. Sci.* 32 (2004) 287–328.

- [2] L. Mater, E.V.C. Rosa, J. Berto, A.X.R. Corrêa, P.R. Schwingel, C.M. Radetski, A simple methodology to evaluate influence of H₂O₂ and Fe²⁺ concentrations on the mineralization and biodegradability of organic compounds in water and soil contaminated with crude petroleum, *J. Hazard. Mater.* 149 (2007) 379–386.
- [3] M. Alcalde, T. Bulter, F.H. Arnold, Colorimetric assays for biodegradation of polycyclic aromatic hydrocarbons by fungal Laccases, *J. Biomol. Screen.* 7 (2002) 547–553.
- [4] A. Napola, M.D.R. Pizzigallo, P. Di Leo, M. Spagnuolo, P. Ruggiero, Mechanochemical approach to remove phenanthrene from a contaminated soil, *Chemosphere* 65 (2006) 1583–1590.
- [5] D.L. McNally, J.R. Mihelcic, D.R. Lueking, Biodegradation of three- and four-ring polycyclic aromatic hydrocarbons under aerobic and denitrifying conditions, *Environ. Sci. Technol.* 32 (1998) 2633–2639.
- [6] A.K. Haritash, C.K. Kaushik, Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): a review, *J. Hazard. Mater.* 169 (1–3) (2009) 1–15.
- [7] K.E. Hammel, B. Kalyanaraman, T.K. Kirk, Oxidation of polycyclic aromatic hydrocarbons and dibenzo[P]-dioxins by phanerochaete-chrysosporium ligninase, *J. Biol. Chem.* 261 (1986) 6948–6952.
- [8] F.D. Kopinke, M. Remmler, Reactions of hydrocarbons during thermodesorption from sediments, *Thermochim. Acta* 263 (1995) 123–139.
- [9] M. Remmler, F.D. Kopinke, Thermal conversion of hydrocarbons on solid matrices, *Thermochim. Acta* 263 (1995) 113–121.
- [10] K.U. Goss, R.P. Schwarzenbach, Adsorption of a diverse set of organic vapors on quartz, CaCO₃, and alpha-Al₂O₃ at different relative humidities, *J. Colloid Interface Sci.* 252 (2002) 31–41.
- [11] C.E. Dowding, M.J. Borda, M.V. Fey, D.L. Sparks, A new method for gaining insight into the chemistry of drying mineral surfaces using ATR-FTIR, *J. Colloid Interface Sci.* 292 (2005) 148–151.
- [12] P.C.D. Milly, A.B. Shmakin, Global modelling of land water and energy balances. Part I. Then land dynamics (LaD) model, *J. Hydrometeorol.* 3 (2002) 283–299.
- [13] C.E. Clarke, F. Kielar, H.M. Talbot, K.L. Johnson, Oxidative decolorization of acid azo dyes by a Mn oxide containing waste, *Environ. Sci. Technol.* 44 (2010) 1116–1122.
- [14] B.J. Reid, G.L. Northcott, K.C. Jones, K.T. Semple, Evaluation of spiking procedures for the introduction of poorly water soluble contaminants into soil, *Environ. Sci. Technol.* 32 (1998) 3224–3227.
- [15] C.T. Chiou, T.D. Shoup, Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity, *Environ. Sci. Technol.* 19 (12) (1985) 1196–1200.
- [16] A.T. Stone, J.J. Morgan, Reduction and dissolution of manganese (IV) oxides by organics. 2. Survey of the reactivity of organics, *Environ. Sci. Technol.* 18 (8) (1984) 617–624.
- [17] T.D. Thompson, W.F. Moll, Oxidative power of smectites measured by hydroquinone, *Clays Clay Miner.* 21 (1973) 337–350.
- [18] S.M. Bamforth, D.A.C. Manning, I. Singleton, P.L. Younger, K.L. Johnson, Manganese removal from mine waters – investigating the occurrence and importance of manganese carbonates, *Appl. Geochem.* 21 (2006) 1274–1287.
- [19] J.L. Junta, M.F. Hochella Jr., Manganese (II) oxidation at mineral surfaces: a microscopic and spectroscopic study, *Geochim. Cosmochim. Acta* 58 (1994) 4985–4999.
- [20] R.J. Bartlett, Characterizing soil redox reactions, in: D.L. Sparks (Ed.), *Soil Physical Chemistry*, CRC Press, Boca Raton, FL, 1999, pp. 371–397.
- [21] B. Raber, I. Kogel-Knabner, C. Stein, D. Klem, Partitioning of polycyclic aromatic hydrocarbons to dissolved organic matter from different soils, *Chemosphere* 36 (1998) 79–97.
- [22] F. Acevedo, L. Pizzul, M.P. Castillo, R. Cuevas, M.C. Diez, Degradation of polycyclic aromatic hydrocarbons by the Chilean white-rot fungus *Anthraco-phyllum*, *J. Hazard. Mater.* 185 (1) (2011) 212–219.
- [23] J.G. Mueller, P.J. Chapman, P.H. Pritchard, Action of a fluoranthene-utilizing bacterial community of polycyclic aromatic hydrocarbon components of creosote, *Appl. Environ. Microbiol.* 55 (1989) 3085–3090.