Chemosphere 189 (2017) 538–546

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Bioconcentration factors and plant–water partition coefficients of munitions compounds in barley

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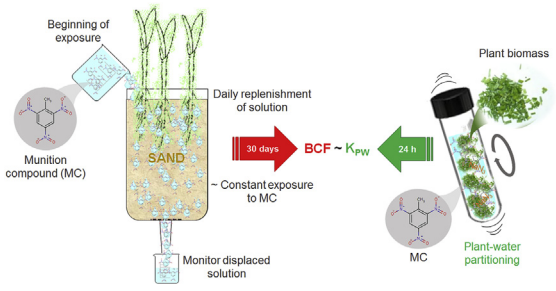
HIGHLIGHTS

- Munitions compounds (MCs) present in growth medium (sand) bioconcentrated in barley.
- Steady state bioconcentration factors achieved; range 0.4 < log (BCF) < 1.3 L kg_{dwt}^{-1}.
- Approximately constant exposure concentrations maintained throughout uptake assays.
- Upper–bounds of BCFs estimated measuring partitioning between barley biomass and water.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 December 2016
Received in revised form
4 September 2017
Accepted 12 September 2017
Available online 14 September 2017

Handling Editor: Jian-Ying Hu

Keywords:
BCF
Partitioning
Plant uptake
Water–sand exposure
Soil

ABSTRACT

Plants growing in the soils at military ranges and surrounding locations are exposed, and potentially able to uptake, munitions compounds (MCs). The extent to which a compound is transferred from the environment into organisms such as plants, referred to as bioconcentration, is conventionally measured through uptake experiments with field/synthetic soils. Multiple components/phases that vary among different soil types and affect the bioavailability of the MC, however, hinder the ability to separate the effects of soil characteristics from the MC chemical properties on the resulting plant bioconcentration. To circumvent the problem, this work presents a protocol to measure steady state bioconcentration factors (BCFs) for MCs in barley (*Hordeum vulgare* L.) using inert laboratory sand rather than field/synthetic soils. Three MCs: 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), and 2,4-dinitroanisole (2,4-DNAN), and two munition–like compounds (MLCs): 4-nitroanisole (4-NAN) and 2-methoxy-5-nitropyridine (2-M-5-NPYNE) were evaluated. Approximately constant plant biomass and exposure concentrations were achieved within a one–month period that produced steady state log BCF values: 0.62 ± 0.02, 0.70 ± 0.03, 1.30 ± 0.06, 0.52 ± 0.03, and 0.40 ± 0.05 L $kg_{plant\ dwt}^{-1}$ for TNT, 2,4-DNT, 2,4-DNAN, 4-NAN, and 2-M-5-NPYNE, respectively. Furthermore, results suggest that the upper–bounds of the BCFs can be estimated within an order of magnitude by measuring the partitioning of the compounds between barley biomass and water. This highlights the importance of partition equilibrium as a mechanism for the uptake of MCs and MLCs by barley from interstitial water. The results from this work provide chemically meaningful data for prediction models able to estimate the bioconcentration of these contaminants in plants.

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https://doi.org/10.1016/j.chemosphere.2017.09.052
0045-6535/

1. Introduction

Elevated concentrations of munitions compounds (MCs) – which include explosives and propellants – have been found in soils at military installations (Simini et al., 1995; Jenkins et al., 2006; Walsh et al., 2007, 2010; Taylor et al., 2015) as well as in underlying groundwater (Spalding and Fulton, 1988; Best et al., 1999a, 1999b; Spiegel et al., 2005; Weeks et al., 2005; Amaral et al., 2009; Clausen et al., 2011) and surrounding surface water bodies (Talmage et al., 1999; Ampleman et al., 2004). MCs dissolve into the soil solution and can be taken up by plants (Cataldo et al., 1990; Groom et al., 2002; McKone and Maddalena, 2007; Panz and Miksch, 2012; Ali et al., 2014). Such mobility makes MCs an environmental concern for organisms growing in the soils at military ranges and surrounding locations. Therefore, risk assessments of these MCs should include an evaluation of their uptake by plants.

The uptake of a chemical substance by plant tissues (e.g., roots, stem, leaves) from the environment (e.g., soil, water, air) has been typically measured by bioconcentration factors (BCFs). BCFs are generally determined through laboratory experiments where plants are grown in spiked or contaminated field soils (Best et al., 2006, 2008; Kobayashi et al., 2008; Rocheleau et al., 2008; Sunahara, 2012) or hydroponically in nutrient solutions containing dissolved contaminants (Li et al., 2002; Su et al., 2009). In the case of solid growth media, various types of BCFs have been used depending on whether expressed relative to the concentration in the medium solids (dry mass) or relative to that in the medium water solution (interstitial/pore water) (McKone and Maddalena, 2007). The latter BCF is chemically more meaningful since the bioavailable fraction is only that dissolved in the interstitial water (Cunningham et al., 1996; Collins et al., 2006). Therefore, BCFs should be calculated as

$$BCF_i = \left(\frac{C_{i_{Organism}}}{C_{i_{Available\ in\ growth\ medium}}}\right)_{SS} = \left(\frac{C_{i_{Plant}}}{C_{i_{IW}}}\right)_{SS} \quad (1)$$

where i = compound of interest (e.g., a MC), BCF_i = bioconcentration factor of i (L_{water} $kg^{-1}_{plant\ dwt}$; dwt = dry weight), SS = steady state, $C_{i_{Plant}}$ = concentration of i in the plant (mg kg^{-1}_{dwt}), and $C_{i_{IW}}$ = dissolved concentration of i in the interstitial water (IW; mg L^{-1}). This BCF definition is used and favored in the review on plant uptake of organic pollutants by McKone and Maddalena (2007). In addition, Eq. (1) is analogous to the extensively used definition for BCF in aquatic systems, which is the ratio of the concentration in the organism to the concentration of the fraction biologically available for uptake in the water (i.e., freely dissolved) (Mackay and Fraser, 2000; Arnot and Gobas, 2006).

Studies have measured uptake by plants from soils at the laboratory scale for some of the most common MCs: 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 2,4-dinitroanisole (2,4-DNAN), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (Groom et al., 2002; Best et al., 2006, 2008; Rocheleau et al., 2008; Sunahara, 2012; Pennington, 1988; Price et al., 2002; Duringer et al., 2010; Chen et al., 2011; Dodard et al., 2013). The set of plant concentrations observed in these soil studies is graphically summarized in Fig. 1A and the data are in Table S1 in Supporting Information (SI). The BCFs are presented in Fig. 1B (SI Table S2) as reported in the corresponding source when available. They are BCFs expressed as the ratio of the MC concentration in the plant to that in the soil solids (this ratio is hereafter referred to as "BCF_{Solids}"). Fig. 1 reveals large variations among both plant concentrations and BCF_{Solids} for a single MC. The variations in plant concentrations are expected since the corresponding exposure concentration is not considered. The variations found in BCF_{Solids} (up to three orders of magnitude for the same MC) for a single MC are likely due to three main factors: plant type, exposure time, and available concentration for plant root uptake. These elements are examined below in order to identify their individual role in the lack of consistency among literature plant uptake results (Fig. 1), especially for BCF_{Solids} (Fig. 1B).

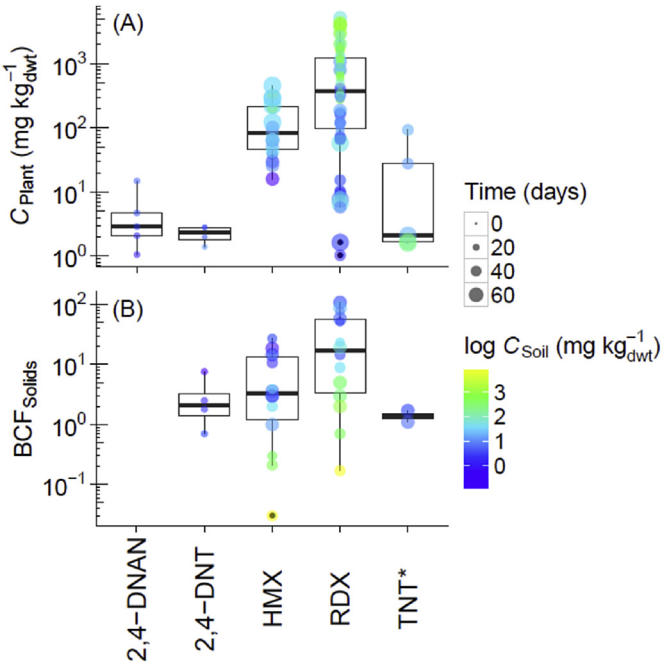

Fig. 1. Results from published uptake studies (SI Tables S1 and S2): (A) MCs concentrations in plants on the last day of exposure (C_{Plant}), and (B) bioconcentration factors expressed relative to concentrations in soil solids (BCF_{Solids}) as kg_{dwt} soil (kg_{dwt} plant)$^{-1}$. C_{Soil}: Concentration in soil at the beginning of exposure. Circles' size proportional to the exposure duration. Data presented for the whole plant or only for the aboveground plant parts when available. TNT* = TNT or TNT degradation products; TNT is reported as not detected in plant tissues in some sources.

Plant type: Some plant species have markedly higher potential to bioconcentrate MCs than others, as it has been shown for aquatic plants relative to terrestrial plants (Panz and Miksch, 2012; Hannink et al., 2002). These differences in uptake potential have not been observed, however, between more similar plant types, such as terrestrial monocotyledons and dicotyledons (Scheidemann et al., 1998). The species included in Fig. 1 are all terrestrial herbaceous plants belonging to closely related families: graminoids (grasses), legumes, and amaryllis. This similarity likely reduces the significance of plant type as a factor for the large BCFs variations shown in Fig. 1.

Exposure time: In contrast to the similarity in plant types, the exposure times in Fig. 1 vary widely from 19 to 77 days. Plant concentrations obtained at longer exposure times (i.e., >40 days) are generally higher than those measured in short–exposure experiments (Fig. 1A). However, these comparisons should only be made once growth dilution effects (Collins et al., 2006) (increasing biomass during the growing period dilutes chemical concentrations in the plant tissues) have been taken into account, concentration in the plant is at steady state (i.e., no significant variations with longer exposure time), and BCFs are reported relative to the bioavailable MC concentration (i.e., BCF defined in Eq. (1) instead of BCF_{Solids}).

Available concentration for plant root uptake: The bioavailable MC concentration in soil for plant uptake is determined by factors including soil properties such as organic carbon content through sorption–desorption processes (Pennington et al., 1995; Larson