Sources and ages of fine-grained sediment to streams using fallout radionuclides in the Midwestern United States

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ABSTRACT

Fallout radionuclides, ^7Be and $^{210}\text{Pb}_{\text{ex}}$, sampled in bed sediment for 99 watersheds in the Midwestern region of the United States and in 15 samples of suspended sediment from 3 of these watersheds were used to partition land from channel sources and to estimate the age or the time since the surface-derived portion of sediment was on the land surface (0 to ~1 year). Channel sources dominate: 78 of the 99 bed material sites (79%) have >50% channel-derived sediment, and 9 of the 15 suspended-sediment samples (60%) have >50% channel-derived sediment. ^7Be was detected in 82 bed sediment samples and all 15 suspended-sediment samples. The surface-derived portion of 54 of the 80 (68%) streams with detectable ^7Be and $^{210}\text{Pb}_{\text{ex}}$ were ≤ 100 days old and the surface-derived portion of all suspended-sediment samples were ≤ 100 days old, indicating that surface-derived fine-grained sediment moves rapidly through these systems. The concentrations of two hydrophobic pesticides –DDE and bifenthrin– are correlated with the proportion of surface-derived sediment, indicating a link between geomorphic processes and particle-associated contaminants in streams. Urban areas had the highest pesticide concentrations and the largest percentage of surface-derived sediment. Although the percentage of surface-derived sediment is less than channel sources at most of the study sites, the relatively young age of the surface-derived sediment might indicate that management actions to reduce sediment contamination where the land surface is an important source could have noticeable effects.

1. Introduction

Increased sediment loading is one of the most common causes for habitat degradation and subsequent loss of stream biological integrity in the United States. In 2014, sediment and turbidity together were the second leading cause, after pathogens, of impairment of U.S. waterways (USEPA, 2014). Excess sediment, in particular the fine-grained fraction (< 63 microns), can alter benthic environments, bury spawning grounds, promote gill damage, attenuate light, and is the vector for sorbed pollutants (Larsen et al., 2010; Owens et al., 2005). Identification of sediment sources is a necessary component supporting effective management actions and policies aimed at reducing sediment inputs (Owens, 2005). Further, determining

the age and residence time of suspended and bed sediment can be useful in estimating the time scales where management actions to reduce sediment might show results.

In general, sediment sources can be delineated into two broad categories: (1) upland or surface sediment sources and (2) non-surface or channel sediment sources (stream banks, bars, and sediment stored in the channel bed). Target sediment is the sediment being sourced and includes suspended sediment, bed sediment, floodplain sediment, and reservoir or lake sediment (Collins and Walling, 2007a,b; Miller et al., 2015). For this study, fine-grained bed material and suspended sediment were the target sediment.

Many sediment-source studies involve sediment budgets or sediment fingerprinting approaches, that are often limited to small geographic areas, generally consisting of a single watershed that is studied over a period of years (Gellis and Walling, 2011; Walling, 2005). This study examined sediment sources at a regional scale, the Corn Belt region (648,239 km²) of the Midwestern United States, during a one-time sampling in the summer of 2013 (Fig. 1). Our hypothesis was that the land surface is a major source of fine-grained sediment to Wadeable streams draining the intensively agricultural Corn Belt region.

In 2013, the U.S. Geological Survey (USGS) National Water Quality Assessment (NAWQA) and the USEPA National Rivers and Streams Assessment (USEPA, 2013) collaborated to assess stream quality across the Midwestern United States (Van Metre et al., 2012). The goal was to characterize water-quality stressors—contaminants, nutrients, sediment, streamflow, and habitat—and ecological conditions in streams across the Midwest Region and to determine the relative effects of these stressors on aquatic organisms. The Midwest Region was selected because it is one of the most intensive and economically important agricultural regions of the country. This paper presents the Midwest Stream Quality Assessment results for fallout radionuclide analysis of sources of bed sediment at 99 stream sites (1 site was not sampled because of high flows) and suspended sediment at 3 sites. The interpretations improve our understanding of sediment sources (surface versus channel) and age fine sediment at a regional scale, both which have important management implications.

1.1. Use of Fallout Radionuclides to Estimate the Source and Age of Sediment

Lead-210 (²¹⁰Pb) (half-life 22.3 years) is a naturally occurring radioactive element in the ²³⁸U decay series. ²³⁸U decays to ²²⁶Ra, which in turn decays to the noble gas ²²²Rn. Some of the ²²²Rn from continental land masses undergoes evasion to the atmosphere, where it ultimately decays to ²¹⁰Pb that attaches to airborne particulates and aerosols. Atmospheric fallout of this ²¹⁰Pb enriches surface soils above the level “supported” by decay of ²¹⁰Ra to ²¹⁰Pb in geologic materials; the unsupported fraction is referred to as excess ²¹⁰Pb (²¹⁰Pb_{ex}). The ²¹⁰Pb_{ex} decays until only the supported ²¹⁰Pb remains, providing a date marker for when surface soils and sediments were last exposed to direct fallout. ²¹⁰Pb_{ex} is primarily delivered to the earth surface in the form of atmospheric aerosols during rainfall events that sorb strongly to fine sediment (Baskaran et al., 1993). The activity of ²¹⁰Pb_{ex} is higher in surface soils relative to streambanks

(Matisoff et al., 2005; Hancock et al., 2014). The activity of $^{210}\text{Pb}_{\text{ex}}$ in surface soils depends on fallout rate and the amount of post-fallout disturbance of the soil. Maximum activities of $^{210}\text{Pb}_{\text{ex}}$ in soils are usually found at the surface and decrease approximately exponentially with depth (Wallbrink et al., 1999), except in cultivated fields where plowing homogenizes $^{210}\text{Pb}_{\text{ex}}$ to the depth of the plow (Matisoff, 2014). The average activity at the watershed scale across a region like the Midwestern U.S. is assumed to be relatively constant because of the continental location of the region (Piliposian and Appleby, 2003).

Beryllium-7 (^7Be) (half-life 53.3 days) is a naturally occurring radionuclide produced in the upper atmosphere by cosmic ray spallation of nitrogen and oxygen. It attaches to airborne particulates and reaches the earth surface mostly through precipitation, where ^7Be -bearing particles sorb to fine sediment (Baskaran et al., 1993). ^7Be is typically found in the top few cm of surface soil (Baskaran et al., 1993). Taylor et al. (2013) provide a useful review of ^7Be and its use in soil and sediment studies.

Both ^7Be and ^{210}Pb have important properties that make them advantageous for sediment-source investigations. They both readily sorb to fine material, which makes them a useful tracer for surface-derived sediment. Because ^7Be and ^{210}Pb are delivered in rainfall, and rainfall delivery on the earth's surface is absent on vertical geomorphic features such as riverbanks, ^7Be and ^{210}Pb are useful tracers to discriminate surface (e.g., topsoil) from non-surface sediment (streambanks and channel bed sediment) (Hancock et al., 2014). Additionally, because ^7Be decays faster (53 days) than $^{210}\text{Pb}_{\text{ex}}$ (22.3 years), decreases in the ratio of $^7\text{Be} : ^{210}\text{Pb}_{\text{ex}}$ can be used to determine the age of sediment (Matisoff et al., 2005; Taylor et al., 2013).

Using the ratios of ^7Be to $^{210}\text{Pb}_{\text{ex}}$ in suspended sediment compared with the ratio in rainfall, Matisoff et al. (2005) developed a model that estimated either the age of suspended sediment (time since the sediment (or soil) was exposed to direct fallout) or the source contribution (surface or channel) to the suspended sediment. Although fluxes of ^7Be and $^{210}\text{Pb}_{\text{ex}}$ vary among rainfall events, the ratio of ^7Be to $^{210}\text{Pb}_{\text{ex}}$ ($^7\text{Be}/^{210}\text{Pb}_{\text{ex}}$) is fairly constant (Matisoff et al., 2005; Wilson et al., 2008). Since ^7Be decays faster than $^{210}\text{Pb}_{\text{ex}}$, a decrease in the ratio of ^7Be relative to $^{210}\text{Pb}_{\text{ex}}$ can be interpreted as an increased age since the rainfall event (Matisoff et al., 2005). Conversely, ^7Be activity is typically higher on surface soils compared to streambanks and the channel bed. Thus lower $^7\text{Be}/^{210}\text{Pb}$ in suspended sediment compared to rainfall is attributed to dilution from source contributions by streambanks and older bed material. Older sediment in this context is defined as greater than one year. Matisoff et al. (2005) acknowledged that his model cannot determine whether lower $^7\text{Be}/^{210}\text{Pb}_{\text{ex}}$ in sediment reflects aging of surface sediment or dilution by older channel sediment.

Matisoff et al. (2005) assumed that the ^7Be and $^{210}\text{Pb}_{\text{ex}}$ activity of the target sediment are related to the rainfall input of ^7Be and ^{210}Pb . Wilson et al. (2008; 2014) observed that the ^7Be activity in surface soil is substantially lower than rainfall inputs. Lower values of ^7Be in soils can be attributed to infiltration, retention by the vegetation canopy, and dilution of rainfall signal

by bioturbation (Taylor et al., 2013; Matisoff, 2014). The same reasoning applies to the $^{210}\text{Pb}_{\text{ex}}$ activity in rainfall, which is higher than the activity of $^{210}\text{Pb}_{\text{ex}}$ in surface soil. Considering that the activity of $^{210}\text{Pb}_{\text{ex}}$ in surface soil builds up an equilibrium activity over the mean life of ^{210}Pb ($1/\lambda$, 32 years), individual rainfall events do not have a marked effect on $^{210}\text{Pb}_{\text{ex}}$ surface activity. Wilson et al. (2014) reported that the $^7\text{Be}/^{210}\text{Pb}_{\text{ex}}$ in surface soils across the U.S. averages 6.7, compared to the average ratio for rainfall ratio of 14.5. Here, we use $^{210}\text{Pb}_{\text{ex}}$ to estimate the fraction of fluvial sediment derived from the land surface and use ^7Be to estimate the time since that surface-derived sediment was on the land surface. The 53-day half-life of ^7Be limits our ability to date the surface-derived component of sediment to about 1 year. Fallout radionuclides ^7Be and $^{210}\text{Pb}_{\text{ex}}$ are delivered by rainfall events with a smaller percentage (~10 %) delivered by dry deposition (Lozano et al., 2011; Taylor et al., 2013). Because we use the soil surface as the target for sourcing and aging sediment, we integrate both wet and dry deposition.

1.2. *Relation of pesticides to surface sediment*

We investigated whether the occurrence of the insecticides bifenthrin and DDE are associated with sites where surface sediment sources dominate, i.e., whether surface-derived streambed sediment has higher bifenthrin and DDE concentrations than channel-derived streambed sediment. Many pesticides, including bifenthrin and DDT, sorb to fine-grained sediment (Amweg et al., 2006; Knezovitch et al., 1987) and can be transported efficiently from the field to the stream (Williamson et al. 1998). Bifenthrin is commonly used in both agricultural and urban settings (Gan et al., 2005). Depending on soil and sunlight conditions, the degradation half-life for bifenthrin ranges from 97 to 345 days (Fecko, 1999). DDT was applied widely throughout the U.S. until its ban in 1972. DDT and its degradation products DDD and DDE are highly insoluble and continue to be widely detected in soil and stream and lake sediment (Nowell et al., 1999; Van Metre and Mahler, 2005). Of DDT, DDE, and DDD, DDE generally dominates in aquatic sediments (Nowell et al., 1999). The half-life of DDE in soil treated one time is 5.7 y, but DDE concentration may not change appreciably with time in soils with repeated DDT applications (Thomas et al., 2008). Although pesticides are associated with agricultural and urban soils, because of their widespread use after World War II (Aspelin, 2003) they are not expected to occur at detectable concentrations in most eroding bank materials, which are composed of older material.

2. Study area

The Midwest Stream Quality Assessment (MSQA) encompassed parts of 12 States in the Midwestern United States (Fig 1) (Van Metre et al., 2012). Climate in the study area ranges from semi-arid in the west to humid continental in the east. Mean annual temperature ranges from 6 to 14°C. Annual precipitation ranges from 69 cm in the west to 130 cm in the east (<http://www.usclimatedata.com/>). Drainage areas for the MSQA sites range from 6.8 to 5893 km², with a median of 167 km², and land uses include row crop, pasture, forest, and urban (Fig. 2A,B; Supplementary Table A). For the entire MSQA region land use is 57% rowcrop, 12% pasture and hay, 10% urban, and the remainder is woodlands and grassland (Supplementary Table A). Underlying geology in the 99 watersheds varies from shale to sandstone to limestone and 2 of the watersheds had some parts underlain by gneiss (Supplementary Table A).

3. Materials and methods

3.1 Collection and Analytical Methods

Bed material was sampled in 99 wadeable streams (Fig. 1) during summer 2013; most sites were sampled in late July and early August. Sites were selected based on the targeted design of the USGS NAWQA Program (e.g., Coles et al., 2012) and the probabilistic design of the USEPA NRSA (Olsen et al., 1999; USEPA, 2013). For each watershed, 20 or more surface (top 2 cm) grab samples were collected from fine-grained channel bed deposits in the sampling reach and composited. MSQA channel reaches ranged from ~150 m to 1600 m, following EPA protocols (Lazorchak, 1998).

Collection of bed material followed the protocol of Shelton and Capel (1994) except that a larger sample volume was collected to allow for multiple analyses. Fine-grained channel bed deposits are typically found in backwater areas and in shallow areas of pools. Care was taken not to sample bed sediment immediately below eroding banks. We consider the fine-grained channel bed deposits to be representative of the watershed sources of sediment (channel and surface-derived sediment).

At three sites (Walnut Creek, IA; Sugar Creek, IN; and Mill Creek, IL; Fig. 1), passive-sampler tubes (Phillips et al., 2000) were placed in the streams for 6 weeks to collect suspended sediment (Fig. 3). Four tubes were mounted in each stream on steel struts in pairs in the center of the channel with the bottom tubes submerged during low flow (Fig. 3). Sediment was retrieved from the passive samplers weekly or shortly after an event and composited.

The bed and suspended-sediment samples were wet sieved with deionized water to <63 microns using polyester sieves. The fine fraction was dried then analyzed for ⁷Be, ²¹⁰Pb, and ²²⁶Ra at the USGS Sediment Radioisotope Laboratory in Menlo Park, California, using a high-resolution gamma spectrometer with an intrinsic germanium detector following methods described in Van Metre et al. (2004, 2007). Measured activities of ⁷Be were corrected for radioactive decay from the date of sample collection to the date of analysis. Excess ²¹⁰Pb is

defined as the difference between the measured total ^{210}Pb and ^{226}Ra . Method detection limits (mdl) for ^7Be and excess ^{210}Pb were 0.4 dpm/g. The sample-specific detection limit for ^7Be was determined by correcting the mdl for decay and varies among samples (0.7 to 1.9 dpm/g) resulting from differing times between sample collection and analysis.

The reported 1-sigma uncertainty in the measured activity (s1) was calculated from the random counting error of samples and background standard spectra at the one standard deviation level. Uncertainty in measured activity was typically within $\pm 10\%$ of the measured activity for total ^{210}Pb and ^{226}Ra , and $\pm 18\%$ for ^7Be . Uncertainty in unsupported ^{210}Pb was propagated from the uncertainties in total ^{210}Pb and ^{226}Ra activity, and averaged $\pm 20\%$.

3.2 Pesticides

Pesticides (including bifenthrin and DDE) were analyzed in the streambed sediment for the 99 watersheds (Supplementary Table D). Samples analyzed for pesticides were unsieved splits of samples collected for radionuclides. Splits for pesticide analysis were placed in baked glass jars and chilled pending analysis. Briefly, sediment samples were extracted by accelerated solvent extraction and the compounds of interest were separated from co-extracted matrix interferences (including sulfur) by passing the extracts through high performance liquid chromatography (HPLC) with gel-permeation chromatography (GPC) along with the use of either stacked graphitized carbon and alumina solid-phase extraction (SPE) cartridges or packed Florisil®. Chromatographic separation, detection, and quantification of the pesticides from the sediment-sample extracts are done by using gas chromatography with mass spectrometry (GC/MS) (Hladik and McWayne, 2012).

3.3 Sediment-Source Allocation

We used a two end-member mixing model using $^{210}\text{Pb}_{\text{ex}}$ to distinguish sediment from surface soils and sediment from banks and older channel deposits (>100 years):

$$f(\text{surf}) = \frac{\text{Pb}}{\text{Pb}(\text{surf})} \times 100 \quad (1)$$

where $f(\text{surf})$ = the percentage of surface-derived sediment; Pb is $^{210}\text{Pb}_{\text{ex}}$ activity in the target sample (dpm/g); Pb(surf) is the land surface (agriculture) $^{210}\text{Pb}_{\text{ex}}$ activity. For this value we relied on published data on $^{210}\text{Pb}_{\text{ex}}$ in agricultural soils (cropland and pasture) from the

literature for the Midwestern U.S. (Supplementary Table B). Because land cover is relatively homogeneous and agricultural, cleared land dominates, and plowed soils are expected to homogenize a fallout constituent, we used the median $^{210}\text{Pb}_{\text{ex}}$ reported in the literature (6.0 dpm/g; Supplementary Table B) to represent surface agricultural soil in the Midwest. The lower endpoint in the model is bank and older channel material that we assumed was free of $^{210}\text{Pb}_{\text{ex}}$ (Wilson et al., 2008) and therefore does not appear in the equation. The mixing model assumes that lower activities of $^{210}\text{Pb}_{\text{ex}}$ are a result of the dilution of recent soil by bank sediment and/or by surface sediment that has been in channel storage for >100 years. Thus when examining sediment sources using $^{210}\text{Pb}_{\text{ex}}$, older sediment, as defined here, is >100 years.

Thus when examining sediment sources using $^{210}\text{Pb}_{\text{ex}}$, older sediment, as defined here, is >100 years. To provide some indication of the effect of uncertainty in the surface-soil $^{210}\text{Pb}_{\text{ex}}$ activity on model results, we also applied the model (eq. 1) using the 25th and 75th percentiles of Pb(surf) (4.0 and 12.6 dpm/g, respectively) (Supplementary Table B).

One limitation of the proportional model is that it cannot distinguish mixing (from surface and channel sources) from radioactive decay in channel deposits. It cannot, for example, determine whether an activity of 3.0 dpm/g is a mixture of 50% recent (i.e., exposed to fallout within the past year or less) agriculture soil and 50% older (>100 years) bank material or a channel deposit that originated from 100% agricultural soil and was isolated from fallout for one $^{210}\text{Pb}_{\text{ex}}$ half-life (22.3 y). We assume that mixing is the more likely scenario, but recognize that radioactive decay might affect the model results by overestimating the fraction of surface sediment.

3.4 Age of sediment

To estimate the activity, and thereby age, of the surface-derived fraction of each sample, we normalized the measured activity by the fraction of the sample estimated to be surface derived, as follows:

$$^7\text{Be}_{(\text{corr})} = \frac{^7\text{Be}}{f(\text{surf})} \quad (2)$$

where $^7\text{Be}_{(\text{corr})}$ is the estimated surface ^7Be activity (dpm/g); ^7Be is the measured ^7Be activity in the target sample (bed material and suspended sediment) (dpm/g); and $f(\text{surf})$ is the percentage of surface-derived sediment derived from equation 1.

Theoretically, $^7\text{Be}_{(\text{corr})}$ adjusts for the dilution of surface-soil activity by ^7Be -free bank material or older (>1 year) channel sediment. The age of the surface-derived fraction of the target sediment is then estimated based on the ratio of the estimated ^7Be surface activity in the target

sample (${}^7\text{Be}_{\text{(corr)}}$; eq. 2) to the 95th percentile of estimated ${}^7\text{Be}$ activity on the surface-derived fraction for all 99 samples, determined as:

$$\text{sed}(\text{age}) = \frac{\text{Ln}\left(\frac{{}^7\text{Be}_{\text{(corr)}}}{{}^7\text{Be}_{(95)}}\right)}{-\lambda_{{}^7\text{Be}}} \quad (3)$$

where $\text{sed}(\text{age})$ is the age of surface-derived sediment (days); ${}^7\text{Be}_{(95)}$ is the 95th percentile of estimated surface ${}^7\text{Be}$ activity; $\lambda_{{}^7\text{Be}}$ is the decay constant for ${}^7\text{Be} = 0.01305/\text{day}$; and ${}^7\text{Be}_{\text{(corr)}}$ is derived from equation 2.

Age as used here means the time since the surface-derived sediment entered the stream and is estimated as the time for decay of surface source activity (${}^7\text{Be}_{95}$) to ${}^7\text{Be}_{\text{(corr)}}$. This approach can date sediment to approximately 1 year old. The age limit of 1 year was determined using the minimum detection limit of ${}^7\text{Be}$ (0.4 dpm/g) for ${}^7\text{Be}_{\text{(corr)}}$ in equation 3. Thus when examining sediment ages using ${}^7\text{Be}$, older sediment, as defined here, is >1 year.

The resulting 95th percentile of estimated surface ${}^7\text{Be}$ activity of soil is 32.5 dpm/g; with ${}^7\text{Be}$ values of 23.3 and 67.2 dpm/g estimated using the 25th and 75th percentile for $\text{Pb}(\text{surf})$ (eq. 1), respectively. Samples with non-detections of ${}^{210}\text{Pb}_{\text{ex}}$ and ${}^7\text{Be}$ were not used in computation of the 95th percentile. The range of values used to estimate ${}^7\text{Be}$ surface soil activities are within reported ${}^7\text{Be}$ activities for surface soils on the Midwest, which ranged from 37.7 to 102 dpm/g (Supplementary Table B).

A limitation of the ${}^7\text{Be}$ age model occurs when surface sediment that is several years old is in channel storage. This sediment will not have ${}^7\text{Be}$ activity, but still will have ${}^{210}\text{Pb}_{\text{ex}}$ activity similar to surface material and, thus, be identified as surface material by the ${}^{210}\text{Pb}_{\text{ex}}$ model (eq. 1). For example, if 100% of the sediment in a sample was surface derived, but 50% is 5 years old, and 50% is 1 day old, the ${}^{210}\text{Pb}_{\text{ex}}$ activity and the fraction percent derived from the land surface would be high ($f(\text{surf}) \sim 1.0$; eq. 1). This leads to minimal correction of ${}^7\text{Be}$ (eq. 2) when, in fact, ${}^7\text{Be}$ should be adjusted by a factor of 2. Thus age-dating of sediment using ${}^7\text{Be}$ in circumstances where surface material has not decayed significantly with respect to ${}^{210}\text{Pb}_{\text{ex}}$ leads to underestimating the surface activity of ${}^7\text{Be}$ and therefore an older age for sediment. The overall result is that the ${}^7\text{Be}$ -based age of the surface material is an upper (older) limit for the age of recent (i.e., less than 1 year) surface material in the sample.

We compare the results of our age-dating model (eq. 3) to the model developed by Matisoff et al. (2005), which uses ${}^7\text{Be}/{}^{210}\text{Pb}_{\text{ex}}$ in rainfall and in the target sample:

$$(4) \quad t = \frac{-1}{(\lambda_{{}^7\text{Be}} - \lambda_{{}^{210}\text{Pb}})} \ln\left(\frac{A}{B}\right) + \frac{1}{(\lambda_{{}^7\text{Be}} - \lambda_{{}^{210}\text{Pb}})} \ln\left(\frac{A_0}{B_0}\right)$$

where t = the age of the target sediment in days; $A = ({}^7\text{Be})$ target sample; $A_o = ({}^7\text{Be})$ rain sample; $B = ({}^{210}\text{Pb}_{\text{ex}})$ target sample; $B_o = ({}^{210}\text{Pb}_{\text{ex}})$ rain sample; and $\lambda_{{}^7\text{Be}}$ and $\lambda_{{}^{210}\text{Pb}}$ are equal to 0.013/day and 8.51×10^{-5} /day, the decay constants for ${}^7\text{Be}$ and ${}^{210}\text{Pb}_{\text{ex}}$, respectively.

Because we did not measure radionuclides in rainfall, we used values reported in the literature for the Midwest (A_o and B_o in equation 4; Supplementary Table C). Using the same approach as for soil radionuclide activities, we took the median ${}^7\text{Be}/{}^{210}\text{Pb}_{\text{ex}}$ for each rainfall study and then took the median of all studies to obtain a ${}^7\text{Be}/{}^{210}\text{Pb}_{\text{ex}}$ for the Midwest of 17.2 (Supplementary Table C)

3.5 Model assumptions

Our analysis is based on a number of assumptions. First, we consider ${}^7\text{Be}$ and ${}^{210}\text{Pb}_{\text{ex}}$ activity as conservative tracers, i.e., their initial activity does not change during erosion and transport in the fluvial system but only by decay and dilution with older sediment (Salant et al., 2007; Wallbrink et al., 1998). Although both ${}^7\text{Be}$ and ${}^{210}\text{Pb}_{\text{ex}}$ have high partition coefficients (K_d values), indicating that they readily sorb to fine-grained soil (You et al., 1989), Taylor et al., (2013) question whether environmental conditions such as reducing, saline, or low pH conditions may effect remobilization. If environmental conditions altered the radionuclide activities in our data set, our interpretations of sources and ages would change, but the direction of this change is indeterminable.

We use ${}^7\text{Be}$ activity as an indicator of the age of surface material. Most of the ${}^7\text{Be}$ activity in surface soils is found in the upper few centimeters (Wilson et al., 2003). Thus we assume that only the topmost surface (~2 cm) is being eroded and deeper erosion of surface soils is not occurring. Deeper surface erosion would tend to lower the ${}^7\text{Be}$ activity in eroded soils, but is assumed not to affect the activity of ${}^{210}\text{Pb}_{\text{ex}}$ appreciably.

We use the 95th percentile of ${}^7\text{Be}$ estimated for the surface-derived portion of the bed sediment (eq. 2) to reflect the surface-soil activity of ${}^7\text{Be}$. Our assumption is that the upper bound activity (95th percentile) in this large sample set is consistent with sites dominated by surface-derived sediment. It was beyond the scope of this study to sample surface soils after individual rainfall events in the study watersheds. However the range of estimated values used for ${}^7\text{Be}$ in surface soil (using the 25th and 75th percentile $\text{Pb}(\text{surf})$ (eq. 1), 23.3 and 67.2 dpm/g, respectively) are reasonable activities relative to a reported range of ${}^7\text{Be}$ in surface soil ranging from 37 to 102 dpm/g (Wilson, 2008, 2014) (Supplementary Table B).

The urban interpretations of sediment sources and ages are based on the ${}^{210}\text{Pb}_{\text{ex}}$ activity in agricultural soils (Supplementary Table B). There may be differences in radionuclide activity related to different soil properties and soil mixing (i.e., plowing) in these settings. Since both land use settings are in the same geographic area (Midwest U.S.), the delivery of ${}^7\text{Be}$ and associated activity may be similar.

Some ^7Be does fall directly on the wetted areas of the stream channels, which might cause an increase in ^7Be activity on sediment already in suspension. It has been estimated that the direct contribution of ^7Be to large rivers (watersheds of 1000s of km^2) could cause a 10–12% increase in measured values, although the authors acknowledge that this estimate might be high (Hancock et al., 2014). Because we did not measure ^7Be in rainfall in the study watersheds we cannot apply correction factors on the direct input of ^7Be to the channel. If rainfall inputs are important, the sediment ages modeled here might be younger than the true ages.

Although target sediment for this study was sieved to <63 microns, the size fraction in which most radionuclide activity occurs, size corrections within this size group were not done. Higher radionuclide activity can be correlated to the finer grain sizes (He and Walling, 1996). Because we used data on fallout radionuclides from other studies, many which do not provide grain size data, we could not normalize our samples by grain size.

Finally, we used a value of zero for $^{210}\text{Pb}_{\text{ex}}$ in bank material. While studies confirm that most streambanks are devoid of $^{210}\text{Pb}_{\text{ex}}$, the surface material of some banks may contain $^{210}\text{Pb}_{\text{ex}}$ activity. If some $^{210}\text{Pb}_{\text{ex}}$ activity occurs in bank material at our sites, our model will over-estimate the surface contribution.

4. Results

Activities of ^7Be and $^{210}\text{Pb}_{\text{ex}}$ in bed and suspended-sediment samples ranged over about 2 orders of magnitude and covary with one another (Fig. 4 and Supplementary Table E). Activities of ^7Be for bed material ranged from non-detect (<0.9 dpm/g) to 90.0 dpm/g and $^{210}\text{Pb}_{\text{ex}}$ from non-detect (<0.4 pm/g) to 31.5 dpm/g. ^7Be and $^{210}\text{Pb}_{\text{ex}}$ were not detected in 17 and 8 samples, respectively, where six of the samples were non detections for both $^{210}\text{Pb}_{\text{ex}}$ and ^7Be . Suspended sediment ^7Be values ranged from 1.6 to 21.7 dpm/g and $^{210}\text{Pb}_{\text{ex}}$ ranged from 0.7 to 6.7 dpm/g (Fig. 4); both radionuclides were detected in all samples.

4.1 Percentage of surface-derived sediment

Non surface-derived sediment or channel sediment is the dominant source of bed sediment for most of the Midwestern streams sampled. The estimated percentage of surface-derived sediment for the 99 bed sediment samples ranged from 0 to 100% with a median value of 29% (Fig. 5A,B); only 21 sites had > 50% surface-derived sediment and only 12 sites had > 70% surface-derived sediment, indicating that most of the bed sediment samples are primarily from bank and channel sources (Fig. 5A,B). The 8 samples in which $^{210}\text{Pb}_{\text{ex}}$ was not detected were assigned a value of 0% surface-derived sediment, and samples with $^{210}\text{Pb}_{\text{ex}}$ activity greater than the soil endpoint were assigned 100% surface-derived sediment. Uncertainty in the model from the choice of $^{210}\text{Pb}_{\text{ex}}$ soil endpoint, indicated by applying the model using the 25th and 75th percentiles of soil $^{210}\text{Pb}_{\text{ex}}$ from the literature, indicates a range for the median surface contribution to bed sediment of 14 to 43% (Fig. 5A,B). Hereinafter, we show results using the median soil $^{210}\text{Pb}_{\text{ex}}$ activities (6.0 dpm/g) in the source model.

The surface-derived fraction of suspended sediment is slightly higher than that of bed sediment (Fig. 5 A,C). Using the median soil $^{210}\text{Pb}_{\text{ex}}$ (6.0 dpm/g) resulted in a median surface fraction of suspended sediment of 38%. Uncertainty in that median surface fraction, based on the 25th and 75th percentile endpoints, was 18 to 57% (Fig. 5C,D). Of the 15 suspended-sediment samples, 6 samples (40%), had greater than 50% surface-derived sediment when using the median soil $^{210}\text{Pb}_{\text{ex}}$ (6.0 dpm/g).

4.2 Age determination of surface derived sediment

An estimate of ^7Be activity in the surface-derived portion of bed and suspended sediment ($^7\text{Be}_{\text{corr}}$) was determined using equation 2 (Supplementary Table E). An estimate of $^7\text{Be}_{\text{corr}}$ was not made for the 19 bed material samples with non-detections for ^7Be and $^{210}\text{Pb}_{\text{ex}}$. Using the calculated surface fraction (eq. 1) based on the median $^{210}\text{Pb}_{\text{ex}}$ soil endpoint, the $^7\text{Be}_{\text{corr}}$ ranged up to 10 times greater than the measured value in the bulk sample (Supplementary Table E).

The ages of the surface-derived fraction of bed sediment estimated from eq. 3 ranged from 0 to 174 days with a median of 82 days (Fig. 6A). Either ^7Be or $^{210}\text{Pb}_{\text{ex}}$ were not detected in 19 samples, and these samples were not used to calculate the median age. Six of these samples were non-detections in both ^7Be and $^{210}\text{Pb}_{\text{ex}}$ and were assigned ages >100 y and were not used to calculate the median values. In two samples, $^{210}\text{Pb}_{\text{ex}}$ was not detected but ^7Be was; the age of these samples could not be determined. Conversely, 11 samples had detectable $^{210}\text{Pb}_{\text{ex}}$ activity with surface-derived sediment of $\geq 13\%$ but ^7Be activity was not detected, indicating that the surface fraction for these samples was older than ~ 1 y. The Matisoff et al. (2005) rainfall model (eq. 4) estimated the range of ages of bed sediment as 61 to 282 days (fig. 6A) with a median age of 172 days. These ages are about twice those estimated using our proportional model resulting from the higher values of both ^7Be and $^{210}\text{Pb}_{\text{ex}}$ in rainfall compared to surface soil.

Suspended-sediment samples were, in general, younger than bed sediment samples (Fig. 6C,D), with an age range of 0 to 84 days (Fig. 6C) and a median of 41 days. Here also, the Matisoff et al. (2005) rainfall model (eq. 4) estimated an older age range: 57 to 174 days (fig. 6C) with a median age of 131 days, and only 33% of the suspended sediment samples had ages less than 100 days. Results of the proportional model indicate that all 15 suspended sediment samples had surface-derived sediment that is less than 100 days old with 60% of the samples with ages less than 50 days (Fig. 6D).

4.3 Relation of sediment sources and ages to land use

Bed-sediment source percentages and ages were examined by land use for each watershed (Fig. 7) (Supplementary Table A). The greatest percentage of surface-derived sediment and the youngest ages of bed sediment were in urban watersheds (Fig. 7A,B). The median percentage

of surface-derived sediment was 93% for urban watersheds, 27 % for agricultural watersheds, and 30% for mixed land-use watersheds (Fig 7A; Supplementary Table F).

The median ages of surface-derived bed sediment for urban, agricultural, and mixed watersheds (includes the four undeveloped watersheds) were 66, 91, and 73 days, respectively (Fig. 7B; Supplementary Table F). Samples with non-detections for ^7Be and with 0% surface-derived sediment were not included in this land use and age analysis. Differences in the median values for the percent of surface-derived and age of bed sediment by land-use types are significantly different (Kruskal-Wallis one-way analysis of variance on ranks test; $p < 0.05$) (Supplementary Table F).

4.3 Relation of sediment sources to pesticide concentrations in bed sediment

Pesticide concentrations of bifenthrin and DDE are highest in those bed-sediment samples with a higher percentage of surface-derived sediment (Fig. 8). The four groups delineated by the percentage of surface-derived sediment are: (1) 0; (2) >0-30%; (3) >30-60%; (4) >60%; differences in the median values between the groups are significant (Kruskal-Wallis one-way analysis of variance on ranks test; $p < 0.05$) (Supplementary Table F). Median concentrations of bifenthrin and DDE are highest in urban areas (Fig. 8C,D); differences in the median values among the land-use groups are significant ($p < 0.05$) for DDE but not bifenthrin (Kruskal-Wallis one-way analysis of variance on ranks test) (Supplementary Table F).

5. Discussion

The majority of the bed and suspended sediment originates from non-surface sediment sources. About three-quarters (79%) of bed-sediment samples contained more than 50% sediment derived from channel sources (banks and bed), and about one-third (30%) of samples contained more than 80% sediment from channel sources (Fig. 5A,B). Because we assume that older channel deposits are free of $^{210}\text{Pb}_{\text{ex}}$, they had to have been isolated from significant atmospheric deposition for about 100 y or more. The majority of suspended sediment also originates from non-surface sources: 60% of samples are >50% channel-derived sediment and 40% are >70 % channel-derived sediment (Fig. 5C,D).

Sediment-source investigations have been done for three of the watersheds sampled here: South Fork Iowa River, Iowa (Wilson et al., 2008); La Sueur River, Minnesota (Belmont et al., 2011); and Walnut Creek, Iowa (Palmer et al., 2014). Estimates of streambank contributions in these studies are similar to estimates of non-surface source contributions presented here for La Sueur and S. Fork Iowa Rivers, and lower than our estimates for Walnut Creek (Supplementary Table G). We do not know how much temporal variability there might be in sediment sources for these sites, but that likely is one reason for the differences indicated for Walnut Creek, Iowa. Other studies in the Midwest have highlighted the importance of bank sediment in the

overall sediment budget. Wilson et al. (2014) reported streambank contributions of 75% for Goodwater Creek, Indiana; Willett et al. (2012) reported that streambank erosion accounted for 79–96% of the total sediment discharge in two watersheds in northeast Missouri.

Although our model cannot differentiate between streambank and sediment that may have been in channel storage for long periods of time (>100 years), samples which have $^{210}\text{Pb}_{\text{ex}}$ activity and no ^7Be activity, are assumed to represent surface-derived sediment that has been in channel storage for at least a year, and perhaps for several decades. Eleven watersheds have bed material with non-detections of ^7Be and detections of $^{210}\text{Pb}_{\text{ex}}$, ranging from 0.6 to 3.2 dpm/g (Supplementary Table E). The surface-derived proportion of sediment for these 11 samples ranges from 10 to 53% and, we conclude, represents surface sediment that has been in channel storage for over one year.

For the three watersheds in this study where bed and suspended sediment were both collected (Fig. 1), $^{210}\text{Pb}_{\text{ex}}$ and ^7Be bed-sediment activities were lower than suspended-sediment activities (Fig. 9A,B). $^{210}\text{Pb}_{\text{ex}}$ in suspended sediment samples was on average 3.3 dpm/g times higher than the bed material sample for Walnut Creek, 1.6 times higher in Sugar Creek, and 1.7 times higher in Mill Creek. ^7Be in suspended sediment samples was on average 4.9 dpm/g times higher than the bed material sample for Walnut Creek, 2.4 times higher in Sugar Creek, and 3.6 times higher in Mill Creek. Higher activities in fallout radionuclides in suspended sediment compared to bed material reflect a greater percentage of surface-derived sediment and younger ages. Similar findings were reported by Matisoff et al. (2005) for sediment from Old Woman Creek, Ohio.

Lower activities in bed sediment relative to suspended sediment and a greater difference between activities of ^7Be than $^{210}\text{Pb}_{\text{ex}}$ in the two target sediment types might be related to two factors: (1) how flow events scour the bed, and (2) sampling depth. Sediment in suspension is a mix of remobilized bed sediment and newly delivered sediment from banks and the land surface. Bed sediment represents a mix of previously deposited material from all sources and likely contains a higher proportion of older, previously deposited sediment than does suspended sediment. The thickness of recently the deposited suspended sediment layer varies with sediment supply, flow, and hydraulic conditions (Lisle and Hilton, 1992). Bed material was sampled from the surface 2-cm of fine sediment deposits. In some cases, the newly deposited sediment may extend deeper and the fallout radionuclide activities of the bed sediment sample matches the activity of the suspended sediment. In cases where recent sediment deposits are thinner than the 2-cm sampling depth, the bed material sampled may include older material. Palazón et al. (2015) evaluated sediment sources for the Isábena River in the Spanish Pyrenees using the sediment-fingerprinting approach and confirmed that bed material reflects long-term trends in sediment sources while suspended sediment reflects short term trends.

The age results of the proportional model used for this study (eq. 3) are systematically younger than those generated by the Matisoff et al. (2005) model (eq. 4), which uses $^7\text{Be}/^{210}\text{Pb}_{\text{ex}}$ in

rainfall (eq. 4). Because rainfall collection was not feasible for the 99 watersheds, we used a value of 17.2 obtained from the literature on rainfall data for the Midwest (Supplementary Table C), which is similar to that reported by Wilson (2014) (14.5) for sites around the U.S. and Matisoff et al. (2005) (16.0) for Old Woman Creek in Ohio. The Matisoff et al. (2005) model estimated ages of bed material that were up to 139 days older than the proportional model (Fig. 6; Supplementary Table E). Because the Matisoff et al. (2005) model uses $^7\text{Be}/^{210}\text{Pb}_{\text{ex}}$ in rainfall, which is higher than the ratio in surface soils (eq. 3), estimated ages are older than those estimated by the proportional model. In addition, the Matisoff model does not adjust for dilution by the older bank material in the sample, which is provided for by the combination of eqs. 1 and 2. The ^7Be and $^{210}\text{Pb}_{\text{ex}}$ activities in rainfall represent the maximum possible activities, yet ^7Be and $^{210}\text{Pb}_{\text{ex}}$ activity decrease once deposited because of dilution from infiltration into the soil, with additional decrease of ^7Be from decay between deposition on the watershed surface and erosion. Because we are interested in determining the surface-soil contribution to stream sediment, and not the rainfall contribution, we chose to use the soil activities as an endpoint.

Studies of the ages of fine-grained bed and suspended sediment are limited for the Midwestern U.S. and for the literature in general. For several watersheds in the Chesapeake Bay, Pizzuto et al. (2014) used a simple mass balance model and estimated travel times for fine-grained sediment of 100 to 1000 years for length scales of 4 to 60 km. For tropical rivers in Mexico, Evrard et al. (2010), using fallout radionuclides, described a 2-box model of sediment residence time: a geologic box, with sediment residence times on the order of thousands of years, and a rapid box, with residence times of 50 to 200 days. The geologic box represents soil erosion rates and flux on hillslopes. The rapid box represents sediment once it reaches the stream. Results shown here for Midwestern streams in the United States show that the surface-derived portion of sediment is relatively young (<100 days), similar to the Evrard et al. (2010)'s rapid box indicating that surface derived fine-grained sediment is moving rapidly through these systems.

We estimated a significantly higher percentage of surface-derived sediment in urban watersheds (44 to 93%) (Fig. 7A,B), with relatively young ages (median 66 days) (fig 8C,D), relative to agricultural watersheds. With greater impervious cover, urban watersheds can deliver sediment efficiently to the channel. Streambank erosion is often a large contributor of sediment in urban watersheds but can be quite variable (Devereux et al., 2010; Smith et al., 2015), accounting for as much as 80% of the total sediment (Allmendinger et al., 2007; Baker et al.; 2015). However, in some urban/suburban watersheds, non-channel sediment (upland and street residue) can be important. In two suburban watersheds in Maryland, 50–67% of the sediment was derived from surface sources (Smith et al., 2015) and in the urban Anacostia River, Maryland and Washington D.C., 42% of the sediment was surface-derived (Devereux et al., 2010). The percentages of surface-derived sediment in urban settings reported here are within values reported by Smith et al. (2015), and are higher than that reported by Devereux et al. (2010).

Pesticide concentrations (bifenthrin and DDE) were higher in watersheds with greater surface-derived source percentages (Fig. 8A,B), and the median concentrations were highest in urban areas (Fig. 8C,D). Although generally higher concentrations of bifenthrin and DDE have been reported to occur in urban settings (Ensminger et al., 2013; Hladik and Kuivila, 2012; U.S. Geological Survey, 1999), sediment sources might also play a role. Bifenthrin and DDE are expected to occur in surface soils, such as agricultural and urban settings (U.S. Geological Survey, 1999; Nowell et al., 2013), (but not in eroding banks and older sediment material. Sediment that is free of $^{210}\text{Pb}_{\text{ex}}$, is not expected to contain modern synthetic organic compounds, in most cases. Thus, regardless of watershed setting or pesticide concentrations in surface soils, occurrence of particle-associated pesticides in streams might be strongly influenced by sediment sources and transport. Our finding that concentrations of bifenthrin and DDE were higher in watersheds with a greater proportion of bed-sediment with a land-surface origin is consistent with this.

The residence times of contaminated sediment determines how quickly sediment moves through the system (Miller et al., 2015) and whether effective management strategies might effectively control this contaminant source (Pizzuto et al., 2014). Management strategies to reduce pesticide fluxes in waterbodies are often directed at reducing non-point source pollution (Kertis and Iivari, 2006; Ribaudo et al., 1999). In this study, higher concentrations of pesticides were measured in surface-derived sediment that also have relatively young ages (< 100 days). Therefore, it might be possible to assess the potential effectiveness of management actions to reduce the erosion and transport of surface derived contaminants using the techniques presented here.

Based on the interpretations presented here, a diagram classifying target sediment by sources and ages is presented (Fig. 10). Increasing $^{210}\text{Pb}_{\text{ex}}$ activity represents a greater contribution of surface sediment and increasing ^7Be activity indicates younger ages (Fig. 10). There are two watersheds in figure 10 where bed sediment showed non detections for $^{210}\text{Pb}_{\text{ex}}$ but contained ^7Be activity. We interpret this as older sediment that has been recently exposed and gained ^7Be activity from rainfall. Recent exposure of older material can occur when streambanks collapse during low flows and are subaerially exposed to rainfall, and subsequently mobilized during the higher flow. Bars in rivers also could be exposed to rainfall during low-flow periods and become mobilized during higher flows (Miller et al., 2015). The six sediment samples in which ^7Be and $^{210}\text{Pb}_{\text{ex}}$ were not detected are interpreted as consisting of streambank material or older material in channel storage. Gully erosion also could produce such activities. In 11 samples, ^7Be activity was not detected but the samples had some $^{210}\text{Pb}_{\text{ex}}$ activity, with 4 of the watersheds having $^{210}\text{Pb}_{\text{ex}}$ activity greater than 1.8 dpm/g. These samples can be interpreted as being dominated by non-surface sources and having some portion of channel deposits that are greater than 1 year old (hence no detectable ^7Be) and younger than about 100 years (hence occurrence of $^{210}\text{Pb}_{\text{ex}}$) (Fig. 10).

6. Conclusions

We use the radionuclide $^{210}\text{Pb}_{\text{ex}}$ (half-life 22.3 years) to determine the percentage of surface-derived sediment and the short-lived radionuclide ^7Be (half-life 53 days) to determine the age of fluvial sediment for 99 dominantly agricultural watersheds in the Midwestern United States. Our model uses the activities of ^7Be and $^{210}\text{Pb}_{\text{ex}}$ in surface soils as endpoints, an improvement over models that use activity in rainfall. The hypothesis that surface soil erosion dominates as a source for fine-grained sediment in Midwestern streams was not supported by this analysis. The major source of sediment to bed and suspended sediment from most watersheds was non-surface sediment: 78 of the 99 sampled streams had 50% or more of the bed sediment derived from streambanks or older channel deposits. Sixty percent of suspended-sediment samples had >50% sediment from channel sources. The surface-derived portion of bed and suspended sediment had relatively young ages; 54 of the 80 (68%) streams with detectable ^7Be and $^{210}\text{Pb}_{\text{ex}}$ activity in bed material had ages that were 100 days or less. All of the suspended-sediment samples had surface-derived sediment fractions that were less than 100 days old. Urban areas had the highest proportion of surface-derived sediment (median of 93%) and the youngest ages of sediment (66 days). With greater impervious cover, urban watersheds are delivering sediment quickly to the channel. Pesticides (bifenthrin and DDE) measured in bed sediment also were highest in urban areas. The lower concentrations of pesticides in sediment from the agricultural basin might be related to the larger contribution of sediment from streambanks which are assumed to not contain synthetic pesticides. Two important findings from this study that have management implications are: (1) the dominant sources of bed sediment and suspended sediment in streams draining agricultural watersheds in the Midwestern United States are streambanks and older channel sediment (>100 years), and (2) the young age of surface-derived sediment (<100 days) indicates that management actions to reduce surface-sediment erosion might be effective in those watersheds with an appreciable surface contribution.

Acknowledgements

We would like to acknowledge USGS NAWQA project staff that assisted in the design and execution of field work including Jeffrey Frey and Amanda Bell, USGS reviewer Chris Konrad, and the USGS Iowa, Indiana, and Illinois Water Science Centers for assistance in the collection of suspended sediment. USGS colleagues also acknowledged are Lisa Nowell for help with pesticide data, Paul Bradley and Lily Gorman-Sanisaca for assistance with the data release, and Naomi Nakagaki for providing GIS analysis and map construction.

Supplementary data related to this article can be found at All_Supplementary_Tables.PDF and data used in analyses presented here for Supplementary Tables D and E are available in machine-readable format at the USGS data release site <https://dx.doi.org/10.5066/F7542KP9>.

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