

# Rapid Release and Changing Sources of Pb in a Mountainous Watershed during Extreme Rainfall Events

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Although atmospheric Pb is known to accumulate in forest soils over time, little is known about the hydrologic Pb export from mountain forest soils. Short-term changes in Pb release and its sources during monsoon rainfall events were investigated in a mountainous watershed in the northern extreme of South Korea by combining intensive storm sampling with measurements of Pb concentrations and isotope ratios in soils and size-fractionated sediments. Biweekly monitoring of forest and agricultural streams showed relatively low dissolved Pb concentrations compared to those found in precipitation. Particulate Pb concentrations in both streams were higher than the dissolved concentrations and increased rapidly during rainfall events. Particulate Pb concentrations were substantially higher in the agricultural stream; the highest concentrations were associated with silt-size sediment followed by sand. A comparison of  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  among sediment fractions and source soils indicated that major sources for silt- and sand-associated Pb in the agricultural stream change between streambank and cropland soils, whereas Pb in the forest stream is primarily derived from forest floors. The results suggest that Pb isotopes can be efficiently applied to tracing short-term changes in sediment and Pb sources and that extreme rainfall events can significantly increase Pb mobilization from erosion-prone mountain soils.

## 1. Introduction

Lead (Pb) is a highly toxic but widely used heavy metal (1). The use of Pb as an antiknock additive in gasoline since the 1930s has resulted in the rapid global distribution of Pb at an unprecedented rate and spatial scale, with evidence of anthropogenic pollution even in remote places such as Greenland and the Arctic (2, 3). Environmental regulations restricting the use of leaded gasoline since the 1970s in the USA and other countries have resulted in a rapid decrease in atmospheric Pb deposition to terrestrial ecosystems (4). Despite recent reductions in atmospheric inputs, large amounts of atmospherically derived Pb have been estimated to remain in forest soils, particularly in organic horizons (4–6).

Many studies have shown a decreasing trend in Pb accumulation in the forest floor in response to decreases in atmospheric deposition since the 1970s (4, 7–9). However,

a closer look at the apparent trends reveals that temporal changes in the concentrations and stocks of Pb in forest floors are highly variable depending on the location, Pb deposition history, and specific organic horizons investigated (7, 10). By comparing the Pb contents in forest floor samples collected from similar locations in Vermont and New York in 1980, 1990, and 2000, Kaste et al. showed that there were no discernible changes in Pb contents at high elevations but found significant decreases in sites at a lower elevation and latitude (10). Decreases in the Pb content at sites with less dense forest floors were ascribed to the enhanced mobility of Pb governed by organic matter decomposition and the colloidal transport of Pb bound to Fe-rich soil particles (10). On the other hand, many studies have assumed either a complete or very high rate of Pb retention in forest soils based on the extremely low dissolved Pb concentrations in streams draining upland forests (6, 9, 11).

Although determining the fate of atmospheric Pb in forest soils requires a more thorough understanding of the mobilization of Pb in both dissolved and particulate phases, little attention has been paid to the hydrologic export of particulate Pb from forest soils. In organic-rich upland watersheds in the UK, the bulk of Pb export via streams has been shown to occur in the particulate phase and mostly under storm conditions (12, 13). In forests the thickness and water penetrability of the forest floor have been suggested to strongly influence Pb retention (10). Considering that intense monsoon rainfalls can facilitate overland flow on steep slopes with a thin, low permeability forest floor (14), Pb mobilization via surface erosion can also occur on steep forested hillslopes, particularly under wet antecedent conditions. In a mountain range river system in France, for example, more than 70% of the annual total Pb export downstream into the estuary occurred in the particulate form, primarily under storm flow conditions that covered less than a month per year (15). Pb mobilization can also substantially increase when forested watersheds undergo a rapid land use change, as shown by the large Pb export from cultivated soils during storm events (16).

Pb isotopes have been widely used to investigate the sources and mobilization pathways of Pb from soils to streamwater (11, 17, 18). However, only a small number of studies have employed Pb isotope analysis for tracing Pb associated with soils eroded from upland systems. For example, a study conducted in a UK upland watershed using measurements of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios for various size fractionations showed that  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in large particulates are similar to those of surface soils but different from those of dissolved and/or colloidal Pb (12). The primary objective of this study was to investigate the hydrobiogeochemical response of soil Pb release to rainfall variability and extremes. Specifically, we used intensive storm sampling in combination with measurements of Pb concentrations and isotope ratios in size-fractionated sediments to examine short-term changes in the magnitude and sources of Pb release from a mountainous watershed undergoing a rapid land use change during monsoon rainfall events.

## 2. Materials and Methods

**2.1. Study Site.** The study was conducted in Haeon Basin (also called the “Punch Bowl Watershed”), which is a bowl-shaped mountainous basin at the northern extreme of South Korea ( $38^{\circ}15'–38^{\circ}20' \text{ N}$ ;  $128^{\circ}05'–128^{\circ}10' \text{ E}$ ; 440 m–1242 m asl; Figure S1), 1–2 km south of the demilitarized zone (DMZ) between South and North Korea. The bedrock in Haeon Basin consists of highly weathered biotite granite at the basin

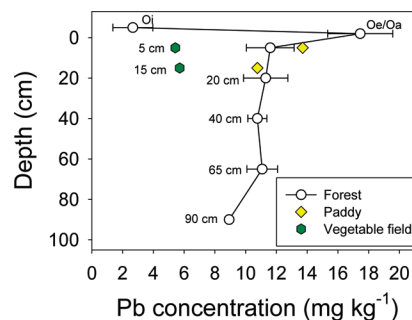
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bottom, surrounded by metamorphic rocks forming mountain ridges (19). Mixed deciduous forests along the mountain ridges and slopes, which have been re-established naturally after the Korean War in the early 1950s and sporadic forest fires in the following two decades, comprise 58% of the whole basin area (60 km<sup>2</sup>). Typical soils in the forested mountain slopes include dry to slightly moist brown soils (Cambisols according to the FAO World Reference Base for Soil Resources) overlain by moder-like forest floors with a distinct Oi horizon and less distinct Oe/Oa horizons. Rapid agricultural expansion in the steep terrain combined with highly erodible soils developed from saprolites across the basin bottom has transformed the basin into a major source of suspended sediments in the North Han River, which supplies drinking water to tens of millions of people living in metropolitan areas.

**2.2. Sampling and Analyses.** Biweekly routine water sampling, combined with intensive storm samplings during the summer monsoon period, was conducted in a headwater stream draining a small forested watershed and a downstream agricultural stream near the outlet of the basin for a 1-year period from May 2008 to April 2009 (Figure S1; refer to the Supporting Information for more details on sampling and chemical analyses). In the forested watershed, the bulk precipitation ( $n = 2$ ), throughfall ( $n = 4$ ), and forest floor leachates (custom-made zero-tension lysimeters;  $n = 6$ ) were also sampled biweekly, along with micrometeorological measurements of the precipitation, air temperature, and soil temperature and volumetric water content at 10 and 30 cm depths. No runoff data were available from the studied steams, so soil–water content data were used to indicate short-term hydrologic responses during rainfall events. Immediately after water sampling, a portion of the sample (10 mL) was filtered onsite using a syringe filter (25 mm Puradisc syringe filter, Whatman; nominal pore size of 0.45  $\mu\text{m}$ ) attached to a 50-mL syringe made of polypropylene and polyethylene (Norm-Jet) based on a simplified filtering method developed for trace metal analysis at remote sites (20). Along with the streambed sediment in the agricultural stream, multiple soil samples were collected at five locations representing major land use types of the basin: an upslope forest, forest streambank, downslope forest, paddy, and vegetable field (Figure S1).

Filtered (0.7  $\mu\text{m}$ ) nonacidified water samples were analyzed for UV absorbance at 254 nm (UVA<sub>254</sub>) and dissolved organic carbon. For total particulate metal analysis, another portion of the water sample was filtered through a polycarbonate filter (0.4  $\mu\text{m}$  pore size; Nuclepore, Whatman) pre-rinsed with dilute HNO<sub>3</sub> and ultrapure water. For the purpose of particle size fractionation, the second and third event samples underwent a three-step sequential filtration using a 60  $\mu\text{m}$  nylon net filter (Millipore) for the sand fraction (apparent size >60  $\mu\text{m}$ ), 2  $\mu\text{m}$  polycarbonate filter (Nuclepore, Whatman) for the silt fraction (2–60  $\mu\text{m}$ ), and 0.4  $\mu\text{m}$  polycarbonate filter (Nuclepore, Whatman) for the clay fraction (0.4–2  $\mu\text{m}$ ).

Both soil samples and suspended sediments collected on the polycarbonate filter were acid-digested using a method modified from Gobeil et al. (21). Dissolved metals including Pb and Pb isotopes (<sup>204</sup>Pb, <sup>206</sup>Pb, <sup>207</sup>Pb, and <sup>208</sup>Pb) in syringe-filtered samples and extracts from acid-digested filters (for particulate metal analysis) were determined with duplicate samples by inductively coupled plasma-mass spectrometry (7500ce ICP-MS, Agilent). Acid digests from silt- and sand-sized sediments along with soil samples were also analyzed for stable Pb isotopes using the same ICP-MS. The relationships between TSS and total metal concentrations were analyzed using a general linear model (SPSS, 2003). The best-fit regression line was drawn only when the regression was statistically significant at  $P < 0.05$ .



**FIGURE 1. Vertical variations in Pb concentrations (mg kg<sup>-1</sup>) for three forest soils, one paddy soil, and one vegetable field soil. Values for forest soils are the mean  $\pm$  one standard deviation of the Pb concentrations at each depth of three different soil profiles.**

### 3. Results and Discussion

#### 3.1. Distribution and Transport of Pb in the Watershed.

Soil Pb concentrations showed distinct vertical differences between the forest floor and mineral soil in the forest (Figure 1). Three forest and one paddy soils exhibited similar concentration ranges at the same depth, with the highest concentrations in the Oe/Oa horizons followed by those of the forest and paddy topsoils. Pb concentrations in the topsoil of a vegetable field were much lower than in other soils and similar to those found for the lower mineral soil horizons of the forest sites, reflecting the fact that mineral soils excavated from deforested hillslopes have been transferred to the vegetable fields over recent years to improve soil fertility in eroding fields.

Biweekly routine monitoring of Pb concentrations in precipitation, forest floor leachates, and streamwaters showed that the volume-weighted annual mean concentrations of ‘dissolved’ (also including colloidal form) Pb were considerably higher throughout the year in the bulk precipitation and throughfall than in the forest floor leachates and both forest and agricultural streams (Table 1). The mean Pb concentration in the precipitation ( $3.12 \pm 3.29 \mu\text{g L}^{-1}$ ) was lower than the pollution level ( $3\text{--}7 \mu\text{g L}^{-1}$ ) reported by Driscoll et al. (22) for industrialized areas of North America a few decades ago, but it was slightly higher than the more recent measurements of Pb concentration in precipitation in the same area (e.g., from  $2.1 \mu\text{g L}^{-1}$  in 1989 to  $0.6 \mu\text{g L}^{-1}$  in 2002 in central Ontario) (9).

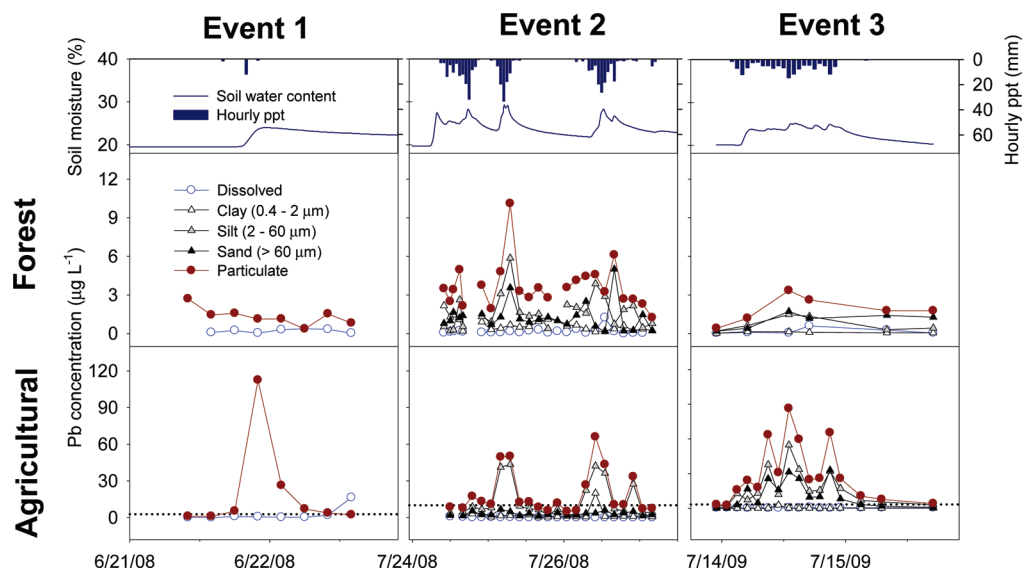
Large decreases in the ‘dissolved’ Pb concentrations from precipitation through forest floor leachates to forest streamwaters observed by the routine monitoring implied high Pb retention in the forest soil and pointed to the forest floor as the main sink of atmospheric Pb and mineral soil as an additional sink; this is consistent with previous studies that reported high Pb retention in forest soils (6, 9, 11). Particulate Pb concentrations were much higher than the ‘dissolved’ concentrations in both the forest and agricultural streams. In both streams, the particulate Pb concentrations tended to be higher during and following storm events. This is likely to be related to the rainfall-induced mobilization of particulate Pb bound to suspended sediments into the stream, as indicated by significant positive relationships between TSS and particulate Pb concentrations ( $r^2 = 0.26$ ,  $n = 20$ ,  $P < 0.05$ ;  $r^2 = 0.70$ ,  $n = 20$ ,  $P < 0.01$  in the forest and agricultural streams, respectively).

**3.2. Short-Term Variations in Streamwater Pb Concentrations during Storm Events.** Intensive storm samplings conducted during three monsoon rainfall events showed rapid changes in the concentrations of ‘dissolved’ and particulate Pb in both the forest and agricultural streams in response to short-term changes in hydrologic conditions; the response magnitudes depended on the site and rainfall

**TABLE 1. Volume-Weighted Mean Concentrations ( $\mu\text{g L}^{-1}$ ) of 'Dissolved' and Particulate (Only for the Forest and Agricultural Streams) Metals in Each Component of the Watershed from May 2008 to April 2009<sup>a</sup>**

compartment	phase	n	$(\mu\text{g L}^{-1})$				
			mean $\pm$ SD	min	max		
bulk precipitation	'dissolved'	11	3.12 $\pm$ 3.29	0.25	(Sep)	8.10	(Nov)
throughfall	'dissolved'	11	2.81 $\pm$ 3.49	0.50	(Sep)	11.9	(Feb)
forest floor leachate	'dissolved'	8	0.77 $\pm$ 0.50	0.40	(Oct)	1.97	(Aug)
forest stream	'dissolved'	19	0.06 $\pm$ 0.13	0.01	(Feb)	0.43	(Sep)
agricultural stream	particulate	20	0.29 $\pm$ 0.16	0.05	(May)	0.53	(Oct)
	'dissolved'	19	0.29 $\pm$ 0.21	0.01	(Mar)	0.81	(Aug)
agricultural stream	particulate	20	2.05 $\pm$ 1.46	0.27	(Jun)	5.19	(Apr)

<sup>a</sup> Values are the mean  $\pm$ 1 standard deviation (SD), followed by minimum (min) and maximum (max) values with relevant months in parentheses.

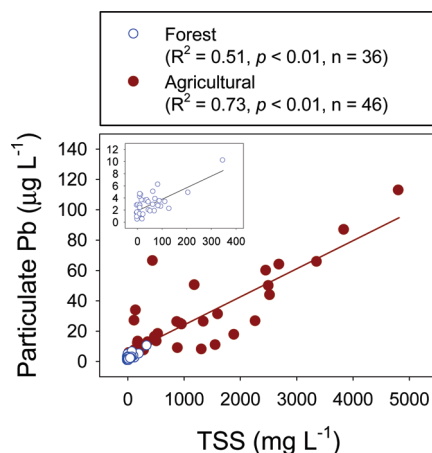


**FIGURE 2. Temporal variations in dissolved and particulate Pb concentrations in the forest and agricultural streams during three storm events. For the second and third event, particulate concentrations were separated into three sediment size fractions: clay, silt, and sand. Dotted lines in the bottom panel represent the maximum concentrations observed in the forest stream.**

intensity and duration (Figure 2). Around the peak flow, particulate Pb concentrations were much higher than 'dissolved' concentrations, and the peak particulate concentrations in the agricultural stream were 1 order of magnitude higher than in the forest stream.

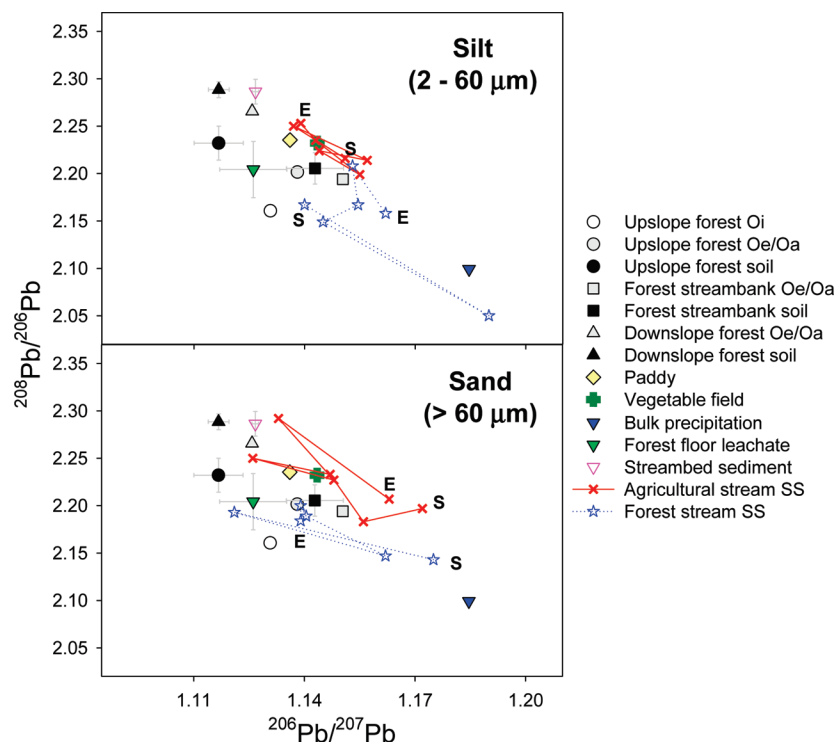
While rainfall-induced increases in particulate Pb concentrations in the forest stream corresponded to rainfall amount and intensity, the highest Pb concentrations in the agricultural stream were observed during the smallest event. Along with the strong positive relationship between TSS and particulate Pb concentrations in the agricultural stream for all three events combined (Figure 3), this suggests that sediment export from croplands may be more strongly influenced by the availability of detachable sediments than rainfall intensity. During the second and third events, which occurred in the later phase of the summer monsoon in both years, the reduced source capacity of highly erodible agricultural soils may have dampened the hydrologic responses for both sediment and particulate Pb export. The weaker responses of sediment-associated Pb to more intense events might be partly related to the dilution of the agricultural runoff by rainwater and streamwaters less enriched with suspended sediments.

In both streams, particulate Pb concentrations associated with silt and sand fractions were much higher than clay-associated Pb concentrations (Figure 2). This was especially true for the silt-associated Pb in the agricultural stream, which comprised the dominant fraction of the particulate Pb concentrations. This result may seem contradictory to recent



**FIGURE 3. Relationships between TSS and particulate Pb concentrations in the forest and agricultural streams during three storm events. The relationship observed in the forest stream is redrawn in the inset for clarity.**

findings emphasizing the enrichment of metals in finer sediments compared to source soils. For example, using experimental erosion plots in the UK, Quinton et al. (16) observed that Pb concentrations were on average 3.3 times higher in eroded sediments than in parent soils and that sediment Pb concentrations were significantly correlated with clay- and silt-sized sediment fractions. When our sediment



**FIGURE 4.** Comparison of the  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios among five soils, rain waters, forest floor leachates, streambed sediments, and suspended sediments sampled during the Event 3. Error bars indicate  $\pm$  one SD. The start and end of the storm event were marked next to each of the corresponding streamwater sediment isotope data with the letters 'S' and 'E', respectively.

Pb data are expressed per unit mass of sediments, the clay-sized sediments had much higher Pb concentrations than those for silt- and sand-associated Pb in both streams (Figure S2). Therefore, high-intensity storms may have facilitated the detachment of heavier sand and silt fractions containing Pb, which dampens the selective enrichment of Pb in finer clay-sized sediments due to the small proportion of clay in the total amount of eroded sediments. A similar predominant distribution of Pb in coarse sediment fractions ( $>25\ \mu\text{m}$ ) was observed during peak flow periods for a small organic-rich upland watershed in Scotland (12).

In contrast to earlier studies reporting near complete retention of atmospheric Pb in the forest floor and upper soil horizons (5, 6), Pb translocation in soils and export to groundwater or surface waters have been found in many different systems (4, 11, 17, 18). Many studies have suggested that the mobility of Pb in soils and streams is primarily controlled by Pb interactions with dissolved or colloidal organic matter (9, 10, 17, 23). Although 'dissolved' Pb concentrations increased slightly under high flow conditions for both the forest and agricultural streams (Figure 2), no significant relationships were found between the 'dissolved' Pb and DOC concentrations. This was presumably due to relatively small changes in very low 'dissolved' Pb concentrations compared to large changes in DOC concentrations during rainfall events (data not shown). In contrast, the strong positive relationship between particulate Pb and TSS concentrations (Figure 3) suggests that Pb release in this watershed is primarily controlled by sediment transport during storms. The dominance of the particulate form in Pb transport has rarely been reported from other forested watersheds, either because particulate Pb was overlooked or because transient, large increases in sediment export during storm events were rarely encountered in most monitoring studies. Similar high rates of sediment-associated Pb release have been observed in highly eroding peatlands (13) or upland systems during storm events (12). For example, Rothwell et

al. found that suspended sediments accounted for 85% of the Pb export from a severely eroding peatland in the UK (13).

**3.3. Tracing Pb Sources Using Pb Isotopes.** The  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios were simultaneously compared between sediment size fractions and source soils to examine the changing contributions of source soils to the release of suspended sediments during the Event 3 (Figure 4). Unlike similar spatial patterns of Pb concentrations observed for five soils excluding that from the vegetable field (Figure 1), simultaneous measurements of  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  enabled source differentiation among the compared soils. The  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios showed differences not only among soils but also along the hydrologic transport pathways of sediments and metals, including the bulk precipitation, forest floor leachates, and streambed sediments (Figure 4). Although significant differences were not established among some of the compared Pb sources (e.g., streambank soils and their neighboring soils), temporally distinct changes in the sediment isotope ratios enabled the comparison of Pb isotope ratios between sediment and source soils as an approach to estimate changing contributions of source soils to the release of sediment-associated Pb over the course of the rainfall event.

The  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios in suspended sediments showed noticeable changes along stream- and fraction-specific trajectories over the course of the rainfall event (Figure 4). Pb isotope ratios for both the silt- and sand-size fractions in the forest stream were usually close to those for Oi and Oe/Oa materials of the forest and streambank, although there were some departures approaching the ratios for precipitation (silt) and forest floor leachate (sand). In the agricultural stream, the isotope ratios of silt-associated Pb were centered around those for streambank and cropland soils, while sand-associated Pb showed a wider trajectory encompassing the ratios of the downslope forest floor and streambed sediments. The Pb isotope ratio values for suspended sediments collected toward the end of events

approached those of the downslope forest floor and streambed sediments, suggesting that these sources might provide additional sand-size sediments during the later phase of the storm event. Considering that sediment Pb isotope ratios might represent a mixture of contributions from different source soils, the proximity between sediment and soil Pb ratios should be used with caution in evaluating source contributions. As sediment source tracing at the watershed scale requires a multitude of geochemical fingerprinting procedures (24, 25), we used our isotope approach not for apportioning exact sediment sources but for examining potential changes in the contribution of major sources to temporal variations in the sediment isotope ratios.

Silt- and sand-size sediments, which comprised the bulk of suspended sediments in both the forest and agricultural streams (Figure 2), showed somewhat different patterns of temporal variations in Pb isotope ratios. In the agricultural stream, the Pb isotope ratios of the silt-size fraction were close to those of the cropland soils, indicating the importance of paddy and vegetable fields as the source of suspended sediments and associated metals in this erosion-susceptible watershed. Pb isotope ratios for sand-size suspended particulate matter approaching those of downslope forest soils and streambed sediments during the later peaks of the intensive storm event pointed to the potential mobilization of heavier sand-size sediments from both streambeds and more sandy soils in the basin bottom compared to the upslope forest. In an agricultural field in UK, Quinton and Catt (16) found that finer clay and silt materials were eroded during small storm events but that larger particles were mobilized during more intense events. In an organic-rich upland watershed in northeast Scotland, Graham et al. (12) found distinct differences in the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio between the 'dissolved' phase and the largest sediment size fraction ( $>25\ \mu\text{m}$ ); the latter determined the isotope ratios for the unfractionated water samples. Since the  $>25\ \mu\text{m}$  fraction contained both silt- and sand-size sediments, their results also emphasized the importance of large particles in transporting Pb, particularly during intensive storm events.

Although a number of studies have applied Pb isotopes to tracking down the sources and transport pathways of Pb in streamwaters (9, 12, 17, 18, 26), there have been few attempts to examine the short-term changes in sediment isotope ratios during storm events. In Thompson Canyon, a subalpine headwater-watershed in Yosemite National Park, Erel and Patterson found similar  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in streamwater to those of the top 2 cm of the soil (17). They suspected that a small portion of anthropogenic Pb may have been released from the upper soil horizons through rain and snowmelt waters during rapid runoff periods primarily attached to colloids or large organic particulates. In the previously mentioned study, Graham et al. (12) also ascribed large increases in streamwater Pb concentration during storm events to the release of anthropogenic Pb accumulated in upper soil horizons. In a small forested watershed in northern Sweden, Klaminder et al. (11) found  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in streamwaters of around 1.18, which suggested that more than 86% of the streamwater Pb was derived from anthropogenic sources given the atmospheric Pb ratio of  $>1.13$  compared to the geogenic Pb ratio of  $>1.5$ .

While these previous studies have focused on demonstrating transfer of anthropogenic Pb from forest soils to streamwaters, our study took the unique approach of measuring short-term changes in Pb isotopes in streamwaters in comparison with those of various source soils. Other studies usually compared sediment isotope ratios with those of two or three parent soils, such as surface soils with higher anthropogenic Pb contents vs less impacted deep soils (9, 11, 12). At larger watershed scales, sediment isotope ratios have been compared with those for a small number of

anthropogenic and natural Pb sources (21, 26). Our results suggest that large spatial variations exist in Pb isotope ratios among soils in mixed-land use watersheds not only vertically but also depending on land use. Simultaneous measurements of three major Pb isotopes for both soils and sediments, combined with intensive storm samplings, can be efficiently used for evaluating temporal changes in relative contributions of the sources and hydrologic transport pathways of Pb.

**3.4. Implications of Rainfall Variability and Extremes for Soil Pb Release.** The overall results suggest that Pb loss from mountain forest soils, especially those associated with suspended sediments, can increase substantially during intense rainfall events. Earlier studies assumed that Pb release is very low in undisturbed forests due to low rates of surface erosion (5, 6). As shown by Pb isotope measurements (Figure 4), the release of easily detachable particles from streambanks or exposed soil surface on steep slopes may have contributed to the unexpectedly high Pb concentrations, even in the forest stream during peak flow periods. More importantly, intense rainfalls may have facilitated the detachment of soil particles from not only highly erodible croplands or streambanks but also litter-covered forest floors.

Rainfall-induced increases in particulate Pb concentrations in the forest stream during rainfall events generally corresponded to the event rainfall amount and intensity, except for the smallest Event 1 (Figure 2). This, along with the positive correlation between TSS and particulate Pb concentrations (Figure 3), suggests that soil erosion in steep mountainous terrain can be an important mobilization pathway for soil Pb during intense rainfall events. Pb mobilization from terrestrial sources has been linked to rainfall patterns either through seasonal comparison of Pb transport at the watershed scale (26) or in intensive storm sampling focusing on short-term concentration changes during storm events (12).

Although large spatiotemporal variations do not allow for an easy generalization of recent trends in precipitation, the frequency and intensity of extreme weather events, particularly heavy rainfalls during the summer monsoon, have increased in many parts of NE Asia (27). Intensifying monsoon rainfalls may result in higher mobilization of soil Pb through rainfall-induced increases in sediments and dissolved organic matter, which have been shown to play a crucial role in watershed-level metal transport (12, 28). Considering the relatively small response of 'dissolved' Pb concentrations to varying rainfall intensities (Figure 2), our results suggest that intensifying rainfall may have greater effects on the mobilization of particulate Pb through the stronger interactions between sediments and Pb. Most current water quality criteria regarding metals are focused on the dissolved phase, assuming high chemical stability and low toxicity of particulate metals. However, transported particulate metals can also pose environmental threats in downstream aquatic systems, because sediment-associated metals can shift partition into the more toxic dissolved phase in response to subtle changes in environmental conditions such as pH, Eh, and DO or upon reaction with other soluble agents (29).

Much higher increases in Pb concentrations in the agricultural stream (Figure 3) corroborate the results from a previous assessment of climate effects on water quality in Northeast Asia; the assessment emphasized that rapid land-use change in steep mountainous regions can substantially increase the vulnerability of soil erosion and associated pollutants to rainfall variability and extremes (30). Since the agricultural stream drains wider and more polluted areas than the forest stream, the relatively high Pb concentrations observed during the peak flow may be attributed to additional Pb inputs from agricultural runoffs or domestic wastewaters. However, similar slopes of the regressions between particu-

late Pb and TSS concentrations in both streams (Figure 3) point to the possibility that increased soil erosion following deforestation on steep hillslopes can result in a drastic increase in the release of Pb that would be otherwise retained in forest soils. As observed in other studies reporting on the high vulnerability of water quality in highly populated areas to climate change (31), our results emphasize that rapid land use change in steep mountain watersheds can increase the vulnerability of water quality to rainfall variability and extremes.

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### Supporting Information Available

Detailed method descriptions on sampling and chemical analyses; Figure S1. Study site and the locations of water (FS: forest stream, AS: agricultural stream) and soil sampling (a: upslope forest, b: forest streambank, c: downslope forest, d: paddy, e: vegetable field); Figure S2. Temporal variations in particulate Pb concentrations expressed per unit mass of suspended sediments ( $\text{mg kg}^{-1}$  sediment) in the forest and agricultural streams during three storm events. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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