Bull. Environ. Contam. Toxicol. (1999) 63:312-319

Bulletin of Environmental Contamination and Toxicology

Surface Water Transport of Lead at a Shooting Range

J. R. Craig,[1] J. D. Rimstidt,[1] C. A. Bonnaffon,[1] T. K. Collins,[2] P. F. Scanlon[3]

[1] Department of Geological Sciences, Virginia Tech, Blacksburg, VA 24061, USA
[2] United States Forest Service, George Washington and Jefferson National Forests, 5162 Vallevoointe Road. Roanoke. VA 24019. USA
[3] Department of Fisheries and Wildlife Science, Virginia Tech, Blacksburg, VA 24061, USA

Received: 1 March 1999/Accepted: 12 July 1999

Lead, one of the earliest metals recognized and used by humans, has a long history of beneficial use to humankind, but has now been recognized as toxic and as posing a widespread threat to humans and wildlife. The adequacy and widespread nature of lead ores (primarily in the forms of the carbonate cerussite, $PbCO_3$, and the sulfide, galena, PbS, combined with its ease of extraction have resulted in the production of more than 300 million metric tons throughout history (Craig, in press). Lead was found to be easily worked, malleable, and slow to corrode relative to iron; hence, it found myriad uses and was the second most used metal (after iron) until being surpassed by copper near the beginning of the 20th Century. The high density, softness and low cost of lead combined with the ease of melting and molding made it the metal of choice for munitions once firearms were developed. Consequently lead, in a wide variety of forms of pellets and bullets, has been expended in warfare, in hunting, and in recreational shooting world wide for hundreds of years. In the United States, the total amount of lead expended as munitions in hunting and recreational shooting has exceeded 3 million metric tons in the 20th Century and is presently increasing at a rate of approximately 60,000 metric tons per year (U.S.G.S. 1998; Craig in press). Hunting tends to spread the lead over wide areas but generally at low concentrations; in contrast, the use of recreational shooting ranges tends to concentrate the lead into much more restricted, but much more heavily lead-loaded areas. As part of a larger study on the nature of lead corrosion and dispersal, the authors have undertaken detailed studies of several shooting ranges in the George Washington and Jefferson National Forests in Southwestern Virginia. This study reports, to the best of our knowledge, the first report of lead concentrations in surface waters draining from an actively used shooting range.

Reports of the toxicity and deleterious effects of lead in the environment on humans date at least as far back as the 16th Century (Agricola as translated by Hoover and Hoover 1950) and these effects are now well documented (Nriagu 1983). Much more recently, Lamphear (1998) summarized problems of human poisoning by lead and specifically pointed to the need to eliminate or control

Correspondence to: J. R. Craig

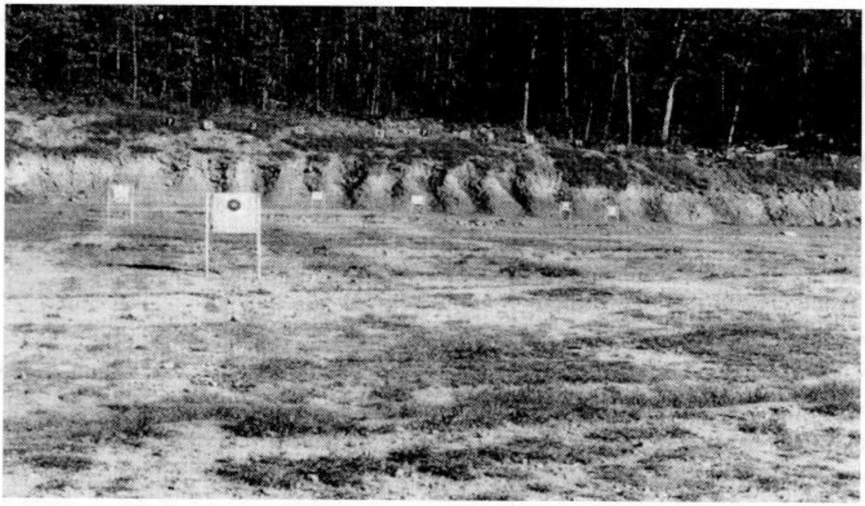

Figure 1. Rifle shooting area of the Blacksburg shooting range. Some of the shallow drainage ditches are visible on the surface of the range and the deeply furrowed portions of the backstop are visible behind the target stands.

possible sources of lead. There has also developed an extensive literature describing the intensity of lead-loading at some hunting and shooting areas and on the widespread impacts of lead on wildlife, especially water fowl (Feierabend 1983; Sanderson and Bellrose, 1986; Pain, 1990; Best et al. 1992; Mateo et al. 1997). Furthermore, in recent years, shooting ranges have been recognized as possible significant point sources of lead and some have been the subject of court actions which forced restriction or closure (Wildlife Management Institute 1995; Riesel and Russo, 1996; Mills, 1997). Recognizing that the American public desires to hunt and conduct recreational shooting and that these activities do disperse lead widely in one case, and locally very heavily in the other case, into the environment, the present study was undertaken to evaluate the degree to which lead is being transported from a highly lead-loaded and actively used shooting range into the surrounding environment.

MATERIALS AND METHODS

The study area is a public shooting range operated by the U.S. Forest Service in the Jefferson National Forest adjacent to Route 621, approximately one-quarter mile (800 meters) north of Route 460 in Montgomery County, Virginia; Latitude 37 18'N, Longitude 80 26'30"W. This area lies in the ultimate headwaters of the James River drainage which terminates in Chesapeake Bay. The shooting range includes two separate shooting areas - (i) rifle range (ii) shotgun range. The rifle range is approximately 100 meters in length and approximately 60 meters in width (Figure 1). It contains sparse grass and slopes upward at about 2 degrees from the shooting stands to the backstop area. The rifle range has been cut into the east side of a forested ridge (known locally as Sinking Creek Mountain). The cut into the ridge provides a backstop which is 2 to 3 meters in height and grades upward several more meters encountering a standing forested slope which continues upward at about a 15 degree angle. The backstop consists of weathered Devonian Brallier Shale with some loose sandstone talus slumping from exposures above. The surface layer of the backstop consists of 10 to 40 centimeters of highly broken and weathered shale which has been fragmented by the large number of bullet impacts. Inspection and digging into the face of the backstop reveals that bullets penetrate up to 50 centimeters where the surface is covered with loose material and up to about 15 centimeters where fresh shale is exposed. The trees in the area above the back stop are 10 to 40 centimeters in diameter. The Forest Service has estimated that there are currently 1 to 3 million rounds expended per year at the Blacksburg Range (W. Compton, U.S. Forest Service, pers. comm. 1998).

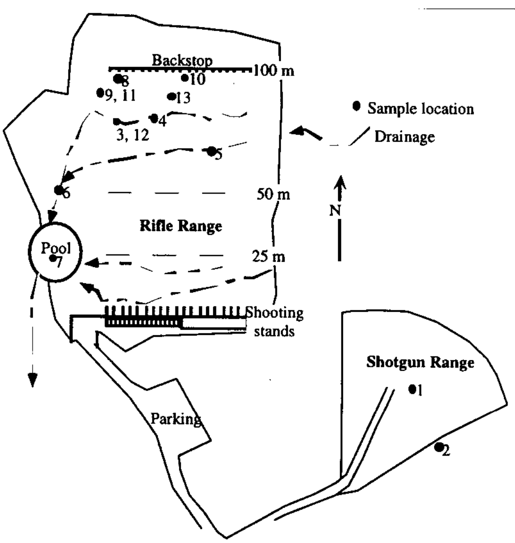

Figure 2. Simple plan map of the Blacksburg shooting range showing the rifle range (rectangular area at the top) and the shotgun range (triangular area at the right). The southeastern face of Sinking Creek Mountain rises upward more than 200 meters in elevation behind the back stop area of the rifle range. This map has been simplified from a large and more detailed map prepared by the U.S. Forest Service. Samples 14 and 15 were taken from 50 m and 75 m down drainage ditch; sample 16 was taken from stream above the confluence with drainage ditch.

The rifle range is traversed by two shallow drainage ditches which extend from right to left and which drain into a longer trough which extends the length of the range on the left side as shown in Figure 2. This drainage ditch terminates in an oval shaped shallow depression which generally contains water up to 1 meter in depth. Water drains out of the shallow depression into a shallow, apparently natural stream bed, parallel to the access road until it passes under the small shooting range access road in a galvanized culvert; the water then passes under Route 621 in another culvert and then into Craig Creek, a tributary of the James River. The distance from the backstop to Craig Creek is more than 400 meters. The face of the earthen backstop is heavily pitted by the impacts of the bullets at the ends of most firing lanes; episodically, ground water drains directly from the pitted face in the areas of bullet impact. During and for variable lengths of time after periods of rainfall, water up to several centimeters in depth is observed draining across the rifle range in the shallow ditches. Several post holes used to support targets and are held open by 4 inch diameter white polyvinyl chloride pipe, are present at variable distances out on the rifle range. These holes were found to commonly contain several centimeters of water. Expended lead munitions and brass shell casings, ranging from 22 to 50 caliber are scattered about the entire rifle range, but bullets are more concentrated in the vicinity of the backstop and casings are more concentrated near the shooting stands.

The shotgun range is a lightly grass covered slope approximately 80 meters in length and 75 meters in width (Figure 2). It drains gently from left to right as viewed from the shooting stands and is subject to sheet flow during periods of rainfall; water periodically stands in a shallow depression in the center of the range approximately 25 meters from the shooting box. There has been only minimal excavation to slightly improve the bowl-like shape of the range; its surface is covered with clay and pebble rich forest soil with no exposure of the underlying shale. Shotgun pellets are scattered throughout but are more concentrated approximately 30 to 50 meters from the shooting stands. There are also numerous plastic cups and pieces of wadding as well as pieces of shattered clay pigeons used for target practice. Expended shotgun shells are numerous near the shooting stands.

Water samples were taken at the sites indicated on Figures 2 and their analyses are tabulated in Table 1. At each site, surface water was captured using a 20 cc syringe, filtered through 0.45 micron nylon filter to remove particulate matter, and then placed into a clean, acid washed, polyethylene bottle. Samples were split with one portion of each being used to determine pH. A test of accuracy was conducted by processing a 50 ppb lead standard solution through an identical filter into a polyethylene bottle; analysis of this sample gave a result of 50.6 ppb. Samples were analyzed using a Perkin-Elmer HGA-600 graphite furnace and a Perkin-Elmer 3300 atomic absorption spectrometer; reported lead values therefore include both dissolved lead as well as lead associated with <0..45 µm particles. Calibration was carried out using commercial standards; the limit of detection was 0.1 ppb.

Several representative bullets were retrieved from the surface and shallow soil at the backstop. These were mounted in cold setting epoxy, cut and polished, and examined using conventional techniques as described by Craig and Vaughan (1994).

Table 1. Analyses of surface waters at the Blacksburg, Virginia shooting range. The sample numbers correspond to the locations shown on Figure 2.

Sample	Lead, ppb	pH	Sample	Lead, ppb	pH
1	17.2	6.41	9	258.5	5.96
2	4.3	6.21	10	290.8	5.28
3	15.1	6.33	11	99.1	5.43
4	134.6	6.18	12	11.7	6.32
5	33.8	6.47	13	473.0	5.47
6	64.6	6.51	14	1.6	6.02
7	22.2	6.50	15	0.3	6.47
8	36.6	6.52	16	0.5	6.35

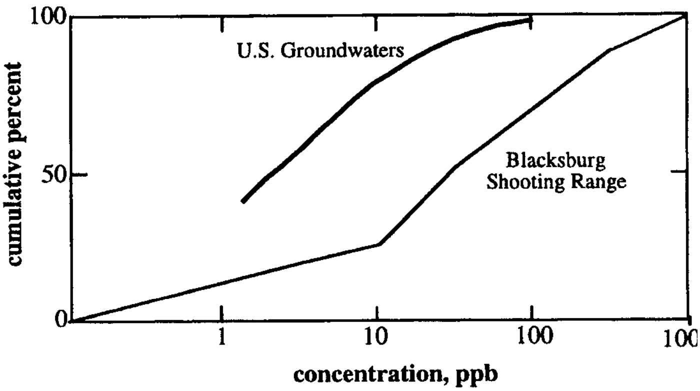

Figure 3. Comparison of water analyses from the Blacksburg shooting range with the lead concentrations of natural ground waters in the United States (based upon Fig. 14.5 in Rose, et al 1969). The displacement of curve of water samples from the Blacksburg shooting range to the right of the overall ground water curve indicates that the shooting range samples contain much higher amounts of lead than do most ground waters.

RESULTS AND DISCUSSION

Sixteen samples of surface waters were taken and analyzed according the procedures described above. The analyses revealed dissolved lead contents ranging from 0.5 to 473 ppb as listed in Table 1. The pH of the solutions ranged from 5.28 to 6.52, typical of the rainfall and of forest surface waters in western Virginia. The locations of the analysis sites is noted on Figure 2. Three sites that were resampled after aproximately 1 month (samples 11 & 9; 12 & 3; and 13 & 10) showed that the observed trends were consistent over time. The data set reveals a general trend with the highest dissolved lead values in the water nearest the backstop, intermediate values on the central parts of the shooting areas and in the draining ditches, and lowest in the streams outside of the boundaries of the shooting area. The four samples taken closest to the backstop gave values ranging from 36.6 to 473 ppb lead. The samples taken in the central parts of the rifle and the shotgun shooting areas gave values ranging from 11.7 to 33.8 ppb lead, one sample taken in the runoff channel at the left margin of the rifle area gave a value of 64.6 ppb lead and the sample from the small collection pond to the left of the rifle area shooting boxes gave a value of 22.2 ppb lead. The sample taken at the margin of the shotgun shooting area where the runoff drains into a natural drainage depression in the forest gave a value of 4.3 ppb lead and the samples taken in the drainage streams approximately 300 meters down stream from the actual shooting areas gave values of 1.6 and 0.3 ppb lead. A sample taken from the small forest drainage stream upstream from the site where it receives drainage from the shooting ranges, and thus presumably where it is unaffected by the shooting range gave a value of 0.5 ppb lead.

The concentrations of lead in natural river waters ranges from 0.6 ppb to 120 ppb with a median value of 5 ppb (Bowen, 1966). Hence, it is not surprising that the lead content of U. S. ground waters display a similar range of concentrations as shown on Figure 3 (Rose et.al. 1969). On this figure we have also plotted the cumulative frequency of lead concentrations that we determined in the waters of the Blacksburg shooting range. The distribution curve for the Blacksburg range samples is shifted upward in concentration by approximately one order of magnitude relative to the curve for the natural ground water samples. This means that while some of the water samples taken from the shooting range have lead contents comparable to natural waters, several of the samples exceed the normal water pattern by as much as 10 times and a few of the samples have values 50 to 100 times the median value for natural waters. Although this pattern is certainly anomalous, it is not clear at this time, whether or not this represents a significant environmental hazard. The Environmental Protection Agency action level for lead in drinking waters is 15 ppb. Only water samples on the range surface or immediately adjacent exceed this value; all waters draining away from the range are far below this threshold. Lead contents of ground waters in the vicinity of the range are not yet known but are now the subject of an ongoing study.

Preliminary examination of representative samples of lead bullets and lead shot from the Blacksburg Shooting range and from other hunting sites has revealed that there are commonly concentric zones of differing corrosion phases. Preliminary identification suggests the presence of lead oxide, $PbsO_4$, around the lead core of the bullet or pellet and a surface layer of lead carbonate an/or hydroxycarbonate. This is similar to the observations of Lin (1996) in the examination of munitions from a shooting range in Sweden and is the subject of continuing study.

The examination of dissolved lead contents in surface waters draining from an actively and heavily used shooting range in the mountains of western Virginia, reveals wide variations in the lead contents of the waters. The samples taken closest to the backstop of the rifle shooting area contained the highest lead values, whereas those taken most distant from the backstop contained the lowest lead

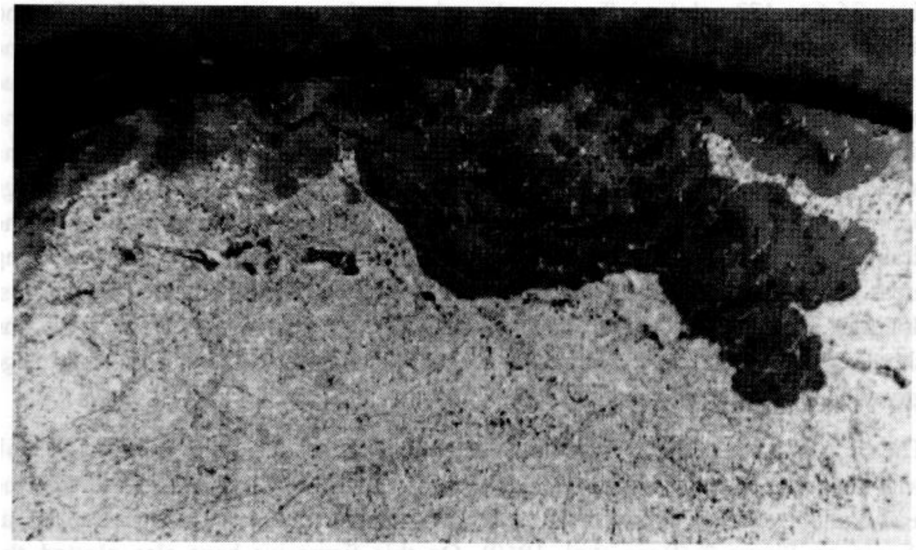

Figure 4. Reflected light photomicrograph of a polished surface cutting through a typical lead bullet collect near site #12 (Figure 2). A rim of corrosion phases, presumably lead hydroxycarbonate, is visible as the gray area just below the surface of the bullet. The liter gray at the bottom of the picture uncorroded metallic lead and the dark area at the top is epoxy. The width of the field of view is 1.2 mm.

values. We interpret this to mean that the higher lead concentrations in the samples from near the backstop result from the constant presence of rapidly corroding fresh lead surfaces which are caused by the impact of the bullets into the soils. Once a passivation layer of lead oxide forms (Figure 4), the dissolution rate of the outermost portion of the munitions is much reduced. Although there is some exposure of fresh lead at nearly all parts of the shooting range because of the impact of bullets, most of the impacts are in the vicinity of the backstop. Most of the expended munitions exposed in central portion of the range have developed passivation layers of oxide and hydroxycarbonate and hence would be expected to be releasing lead into solution at much lower rates. There is not a sufficient increase in the surface flow for dilution to account for a decline in the lead content of the waters. The decline in the lead concentration of the waters as they drain away from the backstop is significant and appears to result from a removal in lead from the waters. The decline in the lead contents of the surface water is important and encouraging because these data suggest that the dispersal of lead from the surface of the shooting range is very small. At the present time, it is not known where the lead that was initially in solution may have gone. Additional studies are being carried out to ascertain what mineralogical phases may have been involved in controlling the lead concentrations; in addition, the lead content of the ground water will be examined.

Acknowledgments. We are indebted to the Service Learning Program at Virginia Tech which provided support for the initial phases of this study. We acknowledge the support of a grant from the Virginia Water Resources and Research Center at Virginia Tech and a participating agreement with the U.S. Forest Service.

REFERENCES

Best TL, Garrison TE, Schmitt CG (1992) Ingestion of lead pellets by scaled quail (*Callipepla squamata*) and northern bobwhite (*Colinus virginianus*) *in* southeastern New Mexico. Texas J Sci 44: 99-107.

Bowen HJM (1966) Trace Elements in Biochemistry. Academic Press, New York.

Craig JR (in press) Metals. In: Giarratano M (ed) Encyclopedia of Global Change. Oxford University Press, New York.

Craig JR, Vaughan DJ (1994) Ore Microscopy and Ore Petrology, 2nd ed. Wiley Interscience, New York, 434 p.

Feierabend JS (1983) Steel shot and lead poisoning in waterfowl. National Wildlife Federation, Scientific and Technical Series 8, 62 p.

Hoover HC, Hoover LH (1950) English translation of De Re Metallica by Georgius Agricola (1556). Dover, New York, 638 p.

Lamphear BP (1998) The paradox of lead poisoning prevention. Science 28: 1617-1618.

Lin Z (1996) Secondary mineral phases of metallic lead in soils of shooting ranges from Obebro County, Sweden. Environ. Geol. 27: 370-375.

Mateo R, Martinez-Vilalta A, Guitart R. (1997) Lead shot pellets in the Ebro delta, Spain: Densities in sediments and prevalence of exposure in waterfowl. Environmental Pollution 96: 335-341.

Mills W (1997) EPA halts all firing at the base. Cape Cod Times, Broken Trust.

Nriagu JO (1983) Lead and Lead Poisoning in Antiquity. John Wiley and Sons, Inc., New York.

Pain DJ (1990) Lead poisoning of waterfowl: A review, in G.V.T. Matthews, ed., Managing Waterfowl Populations, IWRB Special Publication No. 12, 172-181.

Riesel D, Russo S (1996) Minimizing exposure under environmental laws for shooting ranges. In: Peterson RM, Sparrowe RD, Rogers JG (eds) Third National Shooting Range Symposium (Orlando, Florida) 91-97.

Rose AW, Hawkes HE, Webb JS (1969) Geochemistry in Mineral Exploration, 2nd ed. Academic Press, New York, 657 p.

Sanderson GC, Bellrose FC (1986) Lead poisoning in waterfowl. Ill. Nat. Hist. Surv., Spec. Pub. 4, 34 pgs.

USGS (1998) Mineral Industries Survey-Lead 1994 Annual Review. 22 p.

Wildlife Management Institute (1995) Outdoor News Bulletin, Vol. 49, no. 9, p.2.