**Steel Shot as a Risk Factor for Soils at the Area of Shooting Activity**

**Vladimir Lisin, Valentina Chizhikova, Tatiana Lubkovaand Daria Yablonskaya**

Supplementary Materials

# *Table S1. Physiochemical properties of soils*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample | The soil of area  with no prior shooting activities | The soil  of shooting area | The soil of shooting area  with the fertile layer | |
| 0-4 cm | 4-8 cm |
| *The mineral fraction composition* | | | | |
| Quartz (%) | 67.3 | 61.5 | 65.4 | 61.5 |
| Albite (%) | 11.1 | 13.9 | 9.8 | 13.9 |
| Microcline (%) | 9.1 | 8.6 | 5.4 | 8.6 |
| Clay (%) | 9.5 | 8.0 | 10.2 | 8.0 |
| Carbonates (%) | 3.0 | 8.0 | 9.2 | 8.0 |
| Organic carbon (%) | 1.7-2.2 | 1.5-2.5 | 15-17 | 1.5-2.5 |
|  |  |  |  |  |
| pH (1:5 H2O) | 8.1 ± 0.1 | 7.7 ± 0.1 | 8.0 ± 0.1 | 8.0 ± 0.1 |
| EC (µS/cm) | 320 ±20 | 251 ± 40 | 360 ± 20 | 360 ± 20 |
| total Fe (mg kg-1) | 17 400 ± 540 | 21 500 ± 340 | 18 700 ± 210 | 21 500 ± 340 |
| total Pb (mg kg-1) | 26 ± 3 | 3 460 ± 190 | 2 880 ± 120 | 3 460 ± 190 |

# *Table S2. The total iron and total lead in the fine soil fraction (<1 mm) and addition of iron concentration relatively total iron in base soil as a result of steel shot transformation.*

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Humidification regime | Shot | Soil | Depth, cm | Fe, mg kg-1 | | Pb, mg kg-1 |
| mean ± SD | addition | mean ± SD |
| Sub-humid | Mix steel shot and lead shot | **The soil of area with no prior shooting activities** | | | | |
| *base* | *0-8* | *17404 ± 542* | *-* | *26 ± 3* |
|  | | | | |
| after 1 months | 0-4 | 22 910 ± 866 | 5 505 | 2 690 ± 146 |
| 4-8 | 17 069 ± 218 | - | 41 ± 2 |
| after 2 months | 0-4 | 25 230 ± 485 | 7 825 | 4 447 ± 43 |
| 4-8 | 17 005 ± 265 | - | 53 ± 2 |
| after 3 months | 0-4 | 21 855 ± 357 | 4 450 | 2 742 ± 91 |
| 4-8 | 17 269 ±592 | - | 33 ± 4 |
| after 4 months | 0-4 | 21 308 ± 537 | 3 904 | 2 783 ± 70 |
| 4-8 | 17 359 ± 485 | - | 40 ± 4 |
|  | | | | | |
| Steel shot | after 1 months | 0-4 | 21 147 ± 474 | 3 743 | 80 ± 3 |
| 4-8 | 17 139 ± 651 | - | 37 ± 5 |
| after 2 months | 0-4 | 22 793 ± 523 | 5 388 | 90 ± 8 |
| 4-8 | 16 633 ± 450 | - | 35 ± 2 |
| after 3 months | 0-4 | 23 047 ± 456 | 5 642 | 47 ± 2 |
| 4-8 | 17 049 ± 347 | - | 28 ± 2 |
| after 4 months | 0-4 | 22 933 ± 835 | 3 619 | 36 ± 3 |
| 4-8 | 17 411 ± 630 | - | 31 ± 3 |
| **The soil of shooting area** | | | | |
| *base* | *0-8* | *21 497 ± 355* | *-* | *3 458 ± 194* |
|  | | | | |
| after 1 months | 0-4 | 25 689 ± 609 | 4192 | 3 450 ± 144 |
| 4-8 | 21 365 ± 876 | - | 3 330 ± 65 |
| after 2 months | 0-4 | 30 184 ± 995 | 8687 | 3 491 ± 58 |
| 4-8 | 21 537 ± 265 | - | 3 607 ± 118 |
| after 3 months | 0-4 | 27 547 ± 788 | 6050 | 3 326 ± 91 |
| 4-8 | 21 366 ± 904 | - | 3 149 ± 77 |
| after 4 months | 0-4 | 25 421 ± 498 | 3924 | 3 322 ± 85 |
| 4-8 | 21 791 ± 680 | - | 3 811 ± 57 |
|  | | | | |
| Arid | after 1 months | 0-4 | 23 062 ± 689 | 1566 | 3 532 ± 138 |
| 4-8 | 21 756 ± 530 | - | 3 510 ± 219 |
| after 2 months | 0-4 | 24 564 ± 536 | 3067 | 3 441 ± 60 |
| 4-8 | 21 573 ± 536 | - | 3 489 ± 403 |
| after 3 months | 0-4 | 22 696 ± 480 | 1199 | 3 441 ± 104 |
| 4-8 | 21 485 ± 572 | - | 3 397 ± 120 |
| after 4 months | 0-4 | 22 965 ± 471 | 1468 | 3 404 ± 46 |
| 4-8 | 21 633 ± 454 | - | 3 440 ± 48 |
| Humid |  | | | | |
| after 1 months | 0-4 | 23 825 ± 534 | 2328 | 3 469 ± 122 |
| 4-8 | 21 585 ± 864 | - | 3 495 ± 149 |
| after 2 months | 0-4 | 25 296 ± 474 | 3799 | 3 425 ± 172 |
| 4-8 | 21 419 ± 991 | - | 3 427 ± 323 |
| after 3 months | 0-4 | 27 324 ± 631 | 5827 | 3 274 ± 72 |
| 4-8 | 21 499 ± 553 | - | 3 396 ± 110 |
| after 4 months | 0-4 | 30 370 ± 508 | 8873 | 3 537 ± 79 |
| 4-8 | 21 472 ± 432 | - | 3 398 ± 77 |
| **The soil of shooting area with an excess of organic matter** | | | | |
| *base* | *0-4* | *18 714 ± 210* | *-* | *2 882 ± 120* |
| *4-8* | *21 497± 355* | *-* | *3 458 ± 194* |
|  | | | | |
| after 1 months | 0-4 | 25 314 ± 676 | 6 600 | 2 949 ± 151 |
| 4-8 | 21 769 ± 447 | - | 3 539 ± 278 |
| after 2 months | 0-4 | 26 873 ± 678 | 8 159 | 2 956 ± 126 |
| 4-8 | 22 030 ± 830 | - | 3599 ± 100 |
| after 3 months | 0-4 | 27 878 ± 458 | 9 164 | 2 855 ± 211 |
| 4-8 | 21 542 ± 525 | - | 3 606 ± 246 |
| after 4 months | 0-4 | 30 979 ± 501 | 12 265 | 3 306 ± 45 |
| 4-8 | 21 856 ± 436 | - | 3 670 ± 48 |

# *Table S3. Concentrations of dissolved Fe (Fedis <0.45 μm) and of suspended particulate Fe (Fesp)* *in regular filtrates. obtained by interaction "soil:water".*

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Humidi-fication regime | Shot | Soil | Depth profile, cm | рН | σ.  μS cm-1 | Fedis | | Fesp | |
| mg l-1 | % \* | mg l-1 | % \* |
| Sub-humid | Mix steel shot and lead shot | **The soil of area with no prior shooting activities** | | | | | | | |
|  |  |  |  |  |  |  |  |
| after 1 months | 0-8 | 7.0 | 659 | 0.15 | 40 | 0.23 | 60 |
| after 2 months | 0-8 | 7.4 | 223 | 0.05 | 12 | 0.36 | 88 |
| after 3 months | 0-8 | 7.6 | 193 | 0.10 | 29 | 0.24 | 71 |
| after 4 months | 0-8 | 7.7 | 305 | 0.27 | 30 | 0.63 | 70 |
|  | | | | | | | | |
| Steel shot | after 1 months | 0-8 | 7.0 | 791 | 0.19 | 40 | 0.29 | 60 |
| after 2 months | 0-8 | 7.2 | 318 | 0.04 | 10 | 0.37 | 91 |
| after 3 months | 0-8 | 7.6 | 253 | 0.09 | 25 | 0.28 | 75 |
| after 4 months | 0-8 | 7.6 | 280 | 0.15 | 13 | 0.98 | 87 |
| **The soil of shooting area** | | | | | | | |
|  |  |  |  |  |  |  |  |
| after 1 months | 0-8 | 7.6 | 379 | 0.12 | 22 | 0.48 | 78 |
| after 2 months | 0-8 | 7.7 | 203 | 0.06 | 18 | 0.30 | 82 |
| after 3 months | 0-8 | 7.9 | 149 | 0.08 | 21 | 0.31 | 79 |
| after 4 months | 0-8 | 7.8 | 140 | 0.08 | 22 | 0.29 | 78 |
|  |  |  |  |  |  |  |  |  |
| Arid | after 1 months | 0-8 | filtrates were absent throughout the experiment duration | | | | | |
| after 2 months | 0-8 |
| after 3 months | 0-8 |
| after 4 months | 0-8 |
|  |  |  |  |  |  |  |  |  |
| Humid | after 1 months | 0-8 | 7.5 | 259 | 0.05 | 18 | 0.25 | 82 |
| after 2 months | 0-8 | 7.5 | 142 | 0.06 | 18 | 0.25 | 82 |
| after 3 months | 0-8 | 7.7 | 105 | 0.06 | 15 | 0.34 | 85 |
| after 4 months | 0-8 | 7.5 | 127 | 0.05 | 14 | 0.31 | 86 |
| **The soil of shooting area with an excess of organic matter** | | | | | | | |
|  |  |  |  |  |  |  |  |
| after 1 months | 0-8 | 7.1 | 1272 | 0.23 | 69 | 0.10 | 31 |
| after 2 months | 0-8 | 7.2 | 345 | 0.15 | 61 | 0.09 | 39 |
| after 3 months | 0-8 | 7.5 | 173 | 0.12 | 36 | 0.22 | 64 |
| after 4 months | 0-8 | 7.4 | 159 | 0.09 | 48 | 0.09 | 52 |

\* - the relative distribution (%) dissolved Fe and suspended particulate Fe of total in regular filtrates

# *Table S4. Concentrations of dissolved Fe (Fedis <0.45 μm) and of suspended particulate Fe (Fesp) in water extractions (1:5 H2O)*

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Humidi-  fication regime | Shot | Soil | Depth profile, cm | рН | σ.  μS cm-1 | Fedis | | Fesp | |
| mg l-1 | %\* | mg l-1 | %\* |
| Sub-humid | Mix steel shot and lead shot | **The soil of area with no prior shooting activities** | | | | | | | |
| *base* | *0-8* | *8.2* | *340* | *0.06* | *20* | *0.24* | *80* |
|  |  |  |  |  |  |  |  |
| after 1 months | 0-4 | 8.1 | 263 | 0.04 | 8 | 0.39 | 92 |
| after 2 months | 0-4 | 8.2 | 261 | 0.04 | 5 | 0.76 | 95 |
| after 3 months | 0-4 | 8.0 | 230 | 0.02 | 3 | 0.66 | 97 |
| after 4 months | 0-4 | 7.8 | 245 | 0.05 | 7 | 0.66 | 93 |
|  |  |  |  |  |  |  |  |  |
| Steel shot | after 1 months | 0-4 | 8.2 | 286 | 0.05 | 9 | 0.46 | 91 |
| after 2 months | 0-4 | 8.3 | 290 | 0.07 | 13 | 0.47 | 87 |
| after 3 months | 0-4 | 8.3 | 242 | 0.08 | 16 | 0.42 | 84 |
| after 4 months | 0-4 | 7.9 | 261 | 0.06 | 12 | 0.47 | 88 |
| **The soil of shooting area** | | | | | | | |
| *base* | *0-8* | *8.2* | *208* | *0.02* | *14* | *0.13* | *86* |
|  |  |  |  |  |  |  |  |
| after 1 months | 0-4 | 8.2 | 215 | 0.01 | 10 | 0.10 | 90 |
| after 2 months | 0-4 | 8.3 | 220 | 0.03 | 27 | 0.08 | 73 |
| after 3 months | 0-4 | 8.3 | 216 | 0.03 | 24 | 0.09 | 76 |
| after 4 months | 0-4 | 8.2 | 193 | 0.02 | 19 | 0.10 | 81 |
|  |  |  |  |  |  |  |  |  |
| Arid | after 1 months | 0-4 | 7.8 | 139 | 0.01 | 6 | 0.11 | 94 |
| after 2 months | 0-4 | 7.8 | 145 | 0.02 | 4 | 0.49 | 96 |
| after 3 months | 0-4 | 8.0 | 225 | 0.02 | 34 | 0.04 | 66 |
| after 4 months | 0-4 | 7.6 | 223 | 0.05 | 57 | 0.03 | 43 |
|  |  |  |  |  |  |  |  |  |
| Humid | after 1 months | 0-4 | 7.7 | 129 | 0.02 | 6 | 0.24 | 94 |
| after 2 months | 0-4 | 8.0 | 141 | 0.01 | 5 | 0.26 | 95 |
| after 3 months | 0-4 | 7.9 | 203 | 0.02 | 14 | 0.15 | 86 |
| after 4 months | 0-4 | 7.8 | 190 | 0.03 | 48 | 0.03 | 52 |
| **The soil of shooting area with an excess of organic matter** | | | | | | | |
|  |  |  |  |  |  |  |  |
| after 1 months | 0-4 | 8.0 | 247 | 0.05 | 14 | 0.28 | 86 |
| after 2 months | 0-4 | 8.0 | 202 | 0.03 | 21 | 0.11 | 79 |
| after 3 months | 0-4 | 8.1 | 385 | 0.26 | 65 | 0.14 | 35 |
| after 4 months | 0-4 | 7.8 | 335 | 0.12 | 94 | 0.01 | 6 |

\* - the relative distribution (%) dissolved Fe and suspended particulate Fe of total

# *Table S5. Total Fe (Fetot) and its distribution between operationally defined pools: water-soluble (Few). freshly amorphous (hydro)oxides (Feah)and residual (Feres) fractions in the soil*

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Humidi-fication regime | Shot | Soil | *Fetot*.  mg kg-1 | *Few* | | *Feah* | | *Feres* | |
| mg kg-1 | %\* | mg kg-1 | %\* | mg kg-1 | %\* |
| Sub-humid | Mix steel shot and lead shot | **The soil of area with no prior shooting activities** | | | | | | | |
| *base* | *17 404* | *1.5* | *< 0.01* | *3 655* | *21* | *13 749* | *79* |
|  | | | | | | | |
| after 1 months | 22 910 | 2.1 | < 0.01 | 5 040 | 22 | 17 870 | 78 |
| after 4 months | 21 308 | 3.6 | < 0.01 | 4 688 | 22 | 16 620 | 78 |
|  | | | | | | | | |
| Steel shot | after 1 months | 21 147 | 2.5 | < 0.01 | 4 652 | 22 | 16 495 | 78 |
| after 4 months | 22 933 | 2.7 | < 0.01 | 5 275 | 23 | 17 658 | 77 |
| **The soil of shooting area** | | | | | | | |
| *base* | *21497* | *0.8* | *< 0.01* | *3 869* | *18* | *17 628* | *82* |
|  | | | | | | | |
| after 1 months | 25 689 | 0.6 | < 0.01 | 4 881 | 19 | 20 808 | 81 |
| after 4 months | 25 421 | 0.6 | < 0.01 | 5 084 | 20 | 20 337 | 80 |
|  |  | | | | | | | |
| Arid | after 1 months | 23 062 | 0.6 | < 0.01 | 4 843 | 21 | 18 219 | 79 |
| after 4 months | 22 965 | 0.4 | < 0.01 | 4 823 | 21 | 18 142 | 79 |
| Humid |  | | | | | | | |
| after 1 months | 23 825 | 1.3 | < 0.01 | 5 718 | 24 | 18 107 | 76 |
| after 4 months | 30 370 | 0.3 | < 0.01 | 6 681 | 22 | 23 689 | 78 |
| **The soil of shooting area with an excess of organic matter** | | | | | | | |
| *base* | *18 714* | 0.6 | *< 0.01* | *3 930* | *21* | *14 784* | *79* |
|  | | | | | | | |
| after 1 months | 25 314 | 6.5 | 0.03 | 5 316 | 21 | 19 998 | 79 |
| after 4 months | 30 979 | 0.6 | < 0.01 | 6 506 | 21 | 24 473 | 79 |

\* - the relative distribution (%) of total Fe between various pools extracted sequentially.

# *Table S6. The concentration of mobile lead (Pbmob) in soil, water-soluble lead (Pbw) in water extractions from soil (1:5 H2O), the value of the monthly lead removal (*Pbmlr) *obtained by regular filtrates and the water extractions, ratio of dissolved Pb (Pbdis <0.45 μm) and suspended particulate Pb (Pbsp) in regular filtrates, obtained by interaction "soil:water".*

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Humidi-fication regime | Shot | Soil | Pbmob | | | Pbw | | | Pbdis | Pbsp |
| mg kg-1 | | %\* | mg kg-1 | | %\* | %\*\* | %\*\* |
| Sub-  humid | Mix steel shot and lead shot | **The soil of area with no prior shooting activities** | | | | | | | | | |
| *base* | *0.7* | *2.7* | | *0.05* | *0.2* | | 50 | 50 |
|  |  |  | |  |  | |  |  |
| after 1 months | 367 | 14 | | 1.16 | 0.04 | | 50 | 50 |
| after 2 months | 560 | 13 | | 1.56 | 0.04 | | 52 | 48 |
| after 3 months | 311 | 11 | | 1.11 | 0.04 | | 37 | 63 |
| after 4 months | 330 | 12 | | 1.25 | 0.04 | | 19 | 81 |
| Steel shot | **The soil of shooting area** | | | | | | | | | |
| *base* | *113* | *3.3* | | *0.40* | <0.01 | | 40 | 60 |
|  |  |  | |  |  | |  |  |
| after 1 months | 119 | 3.2 | | 0.25 | <0.01 | | 40 | 60 |
| after 2 months | 96 | 2.7 | | 0.18 | <0.01 | | 60 | 40 |
| after 3 months | 100 | 3.0 | | 0.13 | <0.01 | | 53 | 47 |
| after 4 months | 92 | 2.6 | | 0.16 | <0.01 | | 29 | 71 |

\*- a mass fraction Pbmob and Pbw of total Pb in soil.

\*\* - the relative distribution Pbdis and Pbsp of total Pb in regular filtrates