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# Distribution of neptunium and plutonium in New Mexico lichen samples (*Usnea arizonica*) contaminated by atmospheric fallout

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**Abstract** The concentrations of $^{237}$Np, $^{239}$Pu and $^{240}$Pu were determined in lichen samples (*Usnea arizonica*) that were collected from ten locations in New Mexico between 2011 and 2013 using isotope dilution inductively-coupled plasma mass spectrometry (ID-ICP-MS). The observed isotopic ratios for $^{237}$Np/$^{239}$Pu and $^{240}$Pu/$^{239}$Pu indicate trace contamination from global and regional fallout (e.g. Trinity test and atmospheric testing at the Nevada Test Site). The fact that actinide contamination is detected in recent lichen collections suggests continuous re-suspension of fallout radionuclides even 50 years after ratification of the Limited Test Ban Treaty.

**Keywords** $^{237}$Np · Plutonium isotopes · Atmospheric fallout · ICP-MS · Lichen

## Introduction

Lichens obtain essential nutrients directly through atmospheric deposition and have evolved highly efficient mechanisms to bioconcentrate trace elements within their tissues [1]. This characteristic has been used for many years in both Europe and North America to monitor the distribution of atmospheric pollutants [2, 3]. With respect to the Four Corners region of the United States, the pattern of trace, minor, and earth abundant elements measured in the epilithic lichen *Xanthoparmelia* spp. was used to distinguish natural and anthropogenic emissions (agriculture, mining, industrial activities and urban traffic) [4]. This same species was employed by Thomas and Ibrahim to characterize the distribution of plutonium surrounding the Rocky Flats nuclear facility in Colorado [5].

In this paper the lichen *Usnea* spp. was evaluated as a potential biomonitor for trace transuranic contamination. *Usnea* is a widely distributed, yellowish-green fruticose genus of lichen [6]. Occurring within montane regions of Arizona, New Mexico and Colorado, the epiphytic species *Usnea arizonica* (western bushy beard) typically grows on ponderosa and piñon pine trees [7]. Because this species grows several meters above the ground surface, the proposed actinide measurements may reflect regional atmospheric transport (resuspension) rather than superficial contamination from adjacent soils. Studies of this type could find utility in environmental monitoring programs associated with modern nuclear activities [8]. The present work was undertaken to define background concentrations of $^{237}$Np, $^{239}$Pu, and $^{240}$Pu present in samples of *U. arizonica* retrieved from remote locations in New Mexico, USA.

## Experimental

*Usnea Lichen collections* The lichen samples were acquired between June 2011 and November 2013 from forested mountainous regions in New Mexico (Table 1). In general the preferred habitat of *U. arizonica* occurs above 7500 feet in piñon and ponderosa pine forests. However, a sample was also collected from White Rock, NM where the lower elevation corresponds to a generally hotter and drier climate less favorable to this species. At this site *Usnea* sp.

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**Table 1** Lichen collection detail

| Location | Collection Date (mo-yr) | Location (lat; lon) | Elev. (feet) | Dry lichen mass (g) | Lichen ash mass (g) |
|---|---|---|---|---|---|
| Bluewater | Jun-11 | 35°15.939′N; 108°7.089′W | 7509 | 8.1726 | 0.5983 |
| Bluewater | May-13 | 35°15.939′N; 108°7.089′W | 7509 | 13.7708 | 1.0964 |
| Gallinas Peak | Aug-11 | 34°14.815′N; 105°47.309′W | 8633 | 12.6920 | 0.8307 |
| Gallinas Peak | Aug-11 | 34° 14.815′N; 105°47.309′W | 8633 | 9.0595 | 0.6534 |
| Seven Springs | Aug-13 | 35°55.500′N; 106°42.281′W | 7940 | 18.0553 | 0.7909 |
| Norski XC | Oct-13 | 35°47.409′N; 105°48.693′W | 10,340 | 17.3440 | 1.1209 |
| Pajarito Ski Area | Oct-13 | 35°53.685′N; 106°23.853′W | 9510 | 20.0424 | 1.3597 |
| Quemado Lake | Oct-13 | 34°7.793′N; 108°29.878′W | 7899 | 21.3580 | 0.8775 |
| Apache NF | Oct-13 | 34°7.808′N; 108°26.104′W | 8007 | 26.8604 | 1.8111 |
| Carson NF | Oct-13 | 36° 25.270′N; 105°20.600′W | 8986 | 21.7681 | 0.9273 |
| White Rock | Nov-13 | 35°49.038′N; 106°12.743′W | 6435 | 29.4687 | 1.5636 |
| Williams Lake | Nov-13 | 36°34.003′N; 105°25.931′W | 10,800 | 23.3811 | 1.1572 |

was located on piñon trees that were partially protected from the sun on the south side of an east/west trending canyon. The dry mass submitted for analysis varied from $\sim$8 to 29.5 g. Samples were dried, a dry mass recorded, and then ashed at 550° C to provide from $\sim$0.6 to 1.8 g of inorganic residue. The ash was readily dissolved upon repeated fuming with $HNO_3$/HF in a Teflon beaker. After evaporating the acid mixture to dryness a stock solution was prepared with 3 M HCl to which was added $H_3BO_3$ to scavenge fluoride and to facilitate re-dissolution of insoluble $CaF_2$ and $MgF_2$ formed in the HF fuming process.

*ICP-MS instrumentation and operating conditions* Purified samples (vide infra) dissolved in 2 % $HNO_3$ were analyzed using a Thermo *X-series II* quadrupole ICP-MS equipped with an ESI APEX IR sample inlet system. This instrumental configuration provides routine measurement sensitivity of $\sim 3 \times 10^6$ cps/ppb ($^{238}$U). The detector dead time was optimized according to the procedure of Vanhaecke [9] to ensure consistent isotopic ratio measurements. Instrumental mass bias was monitored using the isotopic standards, NBL U500 and CRM 128. The instrumental count rates at mass 237, 239 and 240 amu were measured relative to an internal $^{242}$Pu (NIST SRM 4334G) spike to determine absolute isotopic concentrations and the count rate at mass 238 was monitored to correct for minor interference at mass 239 due to $^{238}U^{1}H$. Results were calculated from the average of 8 replicate analyses. Each replicate (peak hopping mode) represents the average count rate for 800 sweeps (30 ms dwell time for all monitored isotopes). Measurement uncertainty is expressed as 1-sigma standard deviation for the 8 replicate analyses. The uncertainty in absolute $^{239}$Pu concentration includes the NIST certified error in $^{242}$Pu spike concentration. Further details of the operating conditions and instrument performance are provided in Table 2.

*Purification procedure* To the dissolved sample was added a known quantity of $^{242}$Pu (0.7–1.2 $\times 10^{12}$ atoms) tracer that was previously prepared from NIST SRM 4334G. A purified $^{237}$Np/Pu sample was prepared for ICP-MS assay by first pre-concentrating the transuranium elements using a $LaF_3$ precipitation step, followed by anion exchange column chromatography. Details of column preparation, valence adjustment and wash volumes have been previously reported [10]. Minor fractionation of $^{237}$Np and Pu that occurs during the purification process was corrected by measuring the fractionation of an in-house $^{237}$Np/$^{242}$Pu standard that is analyzed in parallel with the environmental samples [10]. Confidence in the analytical procedure was provided through measurements of acid dissolution blanks and laboratory process blanks that were processed in parallel with the lichen samples. From these data an estimated method detection limit of $\sim 5 \times 10^6$ atoms was established. In addition the procedure was used to analyze aliquots of a stock solution of dissolved NIST SRM 4357 (natural matrix radioactivity standard) for $^{237}$Np, $^{239}$Pu, and $^{240}$Pu isotopes. Aliquots of SRM 4357 containing $\sim$0.27 g of dissolved sediment ($\sim 1.6 \times 10^9$ atoms of $^{239}$Pu) were selected for analysis alongside the environmental samples to mimic the concentrations of transuranic isotopes expected in the lichen samples. These quality control results are presented in Table 3 and compare well with previous reports (see [10] and references therein).

## Results

The analytical results of this study are summarized in Table 4. The concentration of $^{239}$Pu measured for each of the *Usnea* spp. lichen samples is presented in units of atoms per gram of lichen ash. This particular convention

**Table 2** Analytical parameters and settings of ICP-MS Xseries II

| Parameters | ICP-MS Xseries II |
|---|---|
| Power | 1400 W |
| Gas flows | Cool gas: 13 L/min |
| | Auxiliary gas: 0.60–0.65 L/min |
| | Nebulizer gas: 0.74-0.78 L/min |
| Sensitivity ($^{238}U$) | $3 \times 10^6$ cps/ppb |
| Backgrounds (2 % $HNO_3$) | <0.5 cps |
| Oxides (Ce) and double charge ions (Ba) | <3 % |
| Sample inlet system | ESI APEX IR |
| Spray and flow rate | Self-aspirating PFA nebulizer: 0.28 mL/min |
| Cones | Ni sample and skimmer cones (Xs) |
| Standard resolution | 0.75 amu (10 % of peak height) |
| $^{238}U^{1}H/^{238}U$ | $3 \times 10^{-5}$ |

**Table 3** Analytical results obtained for ~0.27 g aliquots of NIST SRM 4357

| Sample ID | $^{239}Pu$ (atoms/g sediment) | $^{240}Pu/^{239}Pu$ | $^{237}Np/^{239}Pu$ |
|---|---|---|---|
| 4357-01 | $5.97(10) \times 10^9$ | 0.2369 ± 0.0080 | 0.1512 ± 0.0095 |
| 4357-02 | $5.97(9) \times 10^9$ | 0.2360 ± 0.0093 | 0.1508 ± 0.0085 |
| 4357-03 | $6.02(10) \times 10^9$ | 0.2341 ± 0.0092 | 0.1550 ± 0.0080 |
| 4357-04 | $6.02(10) \times 10^9$ | 0.2285 ± 0.0040 | 0.1469 ± 0.0069 |
| 4357-05 | $5.89(9) \times 10^9$ | 0.2339 ± 0.0086 | 0.1478 ± 0.0071 |
| 4357-06 | $5.94(9) \times 10^9$ | 0.2315 ± 0.0041 | 0.1561 ± 0.0078 |
| Average ± 2σ | $5.97(10) \times 10^9$ | 0.2335 ± 0.0061 | 0.1513 ± 0.0075 |

**Table 4** Concentrations of $^{239}Pu$ and $^{240}Pu/^{239}Pu$ and $^{237}Np/^{239}Pu$ atom ratios for New Mexico *Usnea* spp. lichen samples

| Location | Sample ID | $^{239}Pu$ (atoms/g ash) | $^{240}Pu/^{239}Pu$ | $^{237}Np/^{239}Pu$ |
|---|---|---|---|---|
| Bluewater | BWC-01 | $1.84 (3) \times 10^9$ | 0.1542 ± 0.0047 | Not measured |
| Bluewater | BWC-02 | $1.57 (3) \times 10^9$ | 0.1347 ± 0.0029 | 0.1268 ± 0.0064 |
| Gallinas Peak | GP-01 | $2.42 (4) \times 10^9$ | 0.0919 ± 0.0028 | 0.1466 ± 0.0085 |
| Gallinas Peak | GP-02 | $1.27 (3) \times 10^9$ | 0.0569 ± 0.0047 | 0.0674 ± 0.0071 |
| Seven Springs | SS-01 | $6.39 (2) \times 10^8$ | 0.1187 ± 0.0068 | 0.2480 ± 0.0162 |
| Norski XC | NXC-01 | $1.78 (3) \times 10^9$ | 0.1457 ± 0.0051 | 0.2057 ± 0.0087 |
| Pajarito Ski Area | PSA-01 | $1.12 (2) \times 10^9$ | 0.1548 ± 0.0033 | 0.3556 ± 0.0172 |
| Quemado Lake | QLO-01 | $2.12 (3) \times 10^9$ | 0.1491 ± 0.0046 | 0.2283 ± 0.0110 |
| Apache NF | ANF-01 | $3.15 (7) \times 10^8$ | 0.1331 ± 0.0090 | 0.1723 ± 0.0133 |
| Carson NF | CNF-01 | $2.30 (7) \times 10^8$ | 0.1430 ± 0.0065 | 0.3685 ± 0.0207 |
| White Rock | WR-01 | $1.18 (2) \times 10^9$ | 0.1059 ± 0.0052 | 0.0682 ± 0.0051 |
| Williams Lake Trail | WLT-01 | $2.15 (3) \times 10^9$ | 0.1637 ± 0.0043 | 0.2342 ± 0.0107 |

was chosen to simplify comparison with typical soil analyses. If desired, these data can be expressed in units of atoms per gram of dried lichen using the mass information recorded in Table 1. The transuranic isotopic composition is reported as atom ratios for $^{240}Pu/^{239}Pu$ and $^{237}Np/^{239}Pu$ with associated 1-sigma standard deviation measurement uncertainty.

## Discussion

A number of potential source terms have contributed transuranic isotopes to the environment of New Mexico. The most prominent is Global Fallout due to large thermonuclear tests carried out by both the United States and former Soviet Union [11]. An important regional contributor, especially in the northern mountain areas of the state, is fallout from low yield nuclear tests conducted at the Nevada Test Site (NTS) from 1951 to 1962 [12]. In addition, fallout from the Trinity test (July 1945) extends as a relatively faint plume from ground zero (33° 40.638′N; 106° 28.524′W) to the northeast [13]. Though not detected in this study, reactor derived plutonium due to the Chernobyl (1986) and Fukushima (2011) accidents is also considered [14–16]. Each of these sources is characterized by a unique composition that will ultimately define the isotopic pattern measured in a collection of environmental samples.

The absolute concentration of $^{239}$Pu measured in the *Usnea* sp. lichen samples is broadly comparable to soils in the region. The $^{239+240}$Pu activity concentrations reported by Purtyman, et al. correspond to a $^{239}$Pu concentration range of $3 \times 10^7$–$2 \times 10^9$ atoms/g [17]. The median soil concentration for $^{239}$Pu was $\sim 3 \times 10^8$ atoms/g. Compared to these values the concentration of $^{239}$Pu in lichen ash ranged from $2.3 \times 10^8$ to $2.4 \times 10^9$ atoms/g. The median concentration from this study was $1.4 \times 10^9$ atoms/g, suggesting a possible, admittedly subtle, biological enhancement.

The isotopic composition of the *Usnea* sp. lichen samples are presented in Fig. 1, compared to the three probable source terms. Global Fallout is the best characterized end-member and is indicated by average $^{240}$Pu/$^{239}$Pu and $^{237}$Np/$^{239}$Pu Northern Hemisphere values of 0.180 ± 0.014 and 0.48 ± 0.07, respectively [18]. The isotopic composition of fallout from NTS is more uncertain, not only because of the diversity of experiments [19], but also due to the particular wind and weather conditions at the time of each test [20]. For the purposes of this comparison, a reasonable NTS signature is approximated by $^{240}$Pu/$^{239}$Pu and $^{237}$Np/$^{239}$Pu values of 0.04 and ~0.02, where only one significant figure is justified [18]. Recent measurements of an archived trinitite sample provide an approximation for $^{240}$Pu/$^{239}$Pu and $^{237}$Np/$^{239}$Pu ratios from Trinity fallout of 0.0235 and 0.0021 [21]. The isotopic composition of the lichen collection forms an approximate mixing line between these fallout end-members. The two samples collected from the summit of Gallinas Peak show the strongest contribution from regional fallout. Indeed, Gallinas Peak lies just 57 miles to the northeast of Trinity ground zero, directly under the fallout plume [13]. While the isotopic results for both lichen samples lie on a mixing line between Global Fallout and Trinity fallout, the fact that their individual isotopic compositions are so different from one another (Table 4), suggests the heterogeneous/particulate nature of fallout in the environment. The White Rock lichen sample is unusually low in both $^{237}$Np and $^{240}$Pu concentrations probably reflecting a local signature from historic emissions from the nearby Los Alamos National Laboratory [22].

The eight remaining lichen samples (characterized by $^{240}$Pu/$^{239}$Pu ratios $\geq$0.12) were all collected in remote areas of the state that should not be impacted by local nuclear activities. The isotopic inventory for these samples is considered representative of fallout from both Global and NTS sources. For this group the average $^{240}$Pu/$^{239}$Pu ratio of 0.143 ± 0.028 ($k = 2$) indicates a distinct contribution of transuranium isotopes from low yield tests at NTS, although the $^{237}$Np/$^{239}$Pu ratios are scattered such that an idealized mixing line is not observed. Variation in the $^{237}$Np/$^{239}$Pu ratios could reflect the diversity of fallout from NTS, but more likely results from inter-element fractionation due to natural weathering and redistribution within the environment. For many of the *Usnea* sp. lichen samples, the $^{237}$Np concentration tends to be depleted relative to $^{239}$Pu. Similar behavior has been reported by Lindahl, et al. for *Cladonia stellaris* lichens in Sweden [14]. The isotopic composition of the Swedish samples reflects mixing of Global Fallout with contamination from the Chernobyl accident (Fig. 2). In both the New Mexico and Swedish environments, the $^{237}$Np/$^{239}$Pu ratio tends to be lower than expected for an idealized mixing line. A potential explanation is related to the slightly greater environmental (aqueous) mobility of Np compared to Pu [23]. If Np slightly outstrips Pu in downward migration through the soil column, then the $^{237}$Np/$^{239}$Pu ratio in the

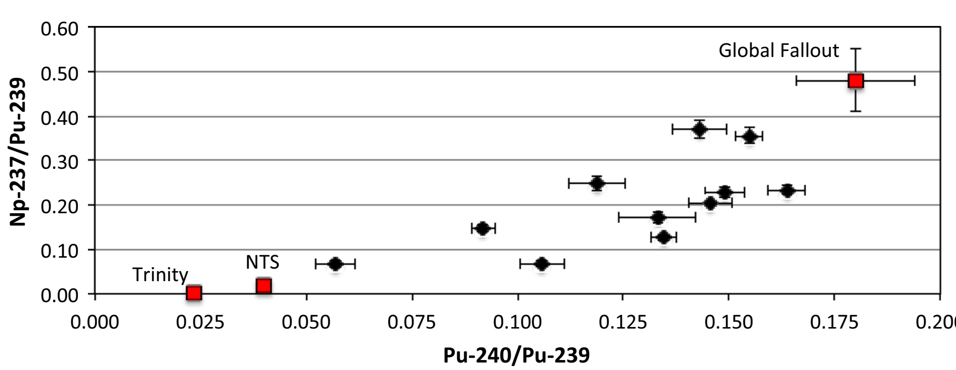


**Fig. 1** A plot of $^{237}$Np/$^{239}$Pu versus $^{240}$Pu/$^{239}$Pu for *Usnea* sp. lichens collected in New Mexico, compared to the isotopic composition of Global Fallout and regional fallout due to testing at the Nevada Test Site (NTS) and the Trinity test

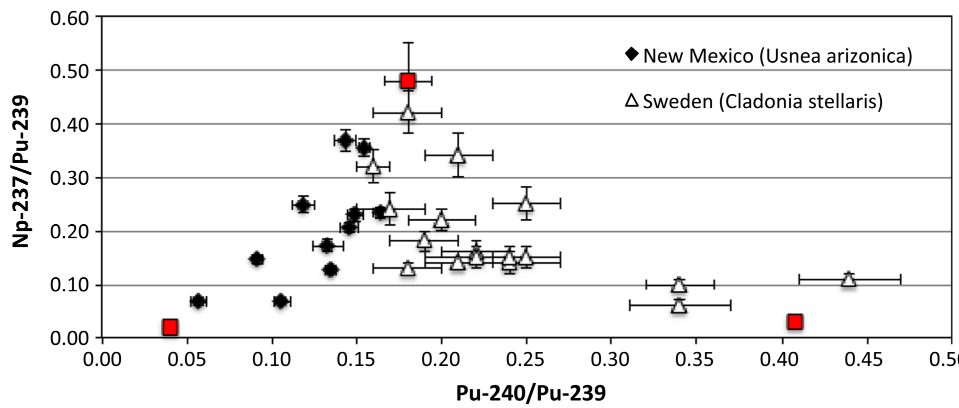


**Fig. 2** Comparison of $^{237}Np/^{239}Pu$ and $^{240}Pu/^{239}Pu$ ratios for New Mexico *Usnea* spp. lichens with Sweden *Cladonia stellaris* lichens

top layer will gradually decline over time [24]. The isotopic composition of transuranic elements measured in lichens is most likely to reflect the uppermost layer of soils that are also the most easily eroded and carried by the wind.

The concentration of contaminants within the tissues of *Usnea* sp. lichens is assumed to be in equilibrium with the environment [1]. The occurrence of transuranic isotopes in modern lichen collections reflects the background concentration of nuclear fallout that is actively moving through wind erosion and atmospheric transport. These processes serve to redistribute and ultimately homogenize one of the most recognizable signatures of the modern era throughout the surface environment of the Earth on very long timescales [25].

## Conclusions

*Usnea* sp. lichens collected from New Mexico contain transuranic isotopes derived from historic atmospheric nuclear fallout. The concentration of $^{237}Np$, $^{239}Pu$ and $^{240}Pu$ in lichen ash samples is comparable or slightly elevated compared to regional soils. The isotopic composition of the transuranic contamination reflects mixtures of Global Fallout and regional fallout from the Nevada Test Site (NTS) and from the Trinity test. The fact that contamination is detected in recent lichen collections suggests continuous re-suspension of fallout radionuclides even 50 years after ratification of the Limited Test Ban Treaty.

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