

Supporting Information for:

Trace metal content of coal exacerbates air pollution-related health risks: the case of lignite coal in Kosovo

Noah Kittner^{a,b,c}, Raj P. Fadadu^c, Heather L. Buckley^{c,d}, Megan R. Schwarzman^{c,e}, and
Daniel M. Kammen^{a,b,f,*}

^a Energy and Resources Group, UC Berkeley, Berkeley, CA 94720

^b Renewable and Appropriate Energy Laboratory, UC Berkeley, Berkeley, CA 94720

^c Berkeley Center for Green Chemistry, UC Berkeley, Berkeley, CA 94720

^d Energy Technologies Area, Lawrence Berkeley National Lab 94720

^e Center for Occupational and Environmental Health, UC Berkeley, CA 94720

^f Goldman School of Public Policy, UC Berkeley, Berkeley, CA 94720

*Address correspondence to: kammen@berkeley.edu

Summary Contents (9 pages)

List of Figures:

Figure S1. Map of lignite coal mine in Obilic, Kosovo located 12 km from Pristina.

Figure S2. Projected sources of energy generation in a business as usual path that includes the development of Kosovo C.

Figure S3. Projected sources of electricity generation in a Euro 2030 path met with energy efficiency measures, 27% CO₂ emission reduction, >27% renewable consumption, expanded power exchange for imports

Figure S4. Projected sources of electricity generation in a low-cost solar pathway without flexible natural gas

Figure S5. Projected sources of electricity generation in a low-cost solar pathway with flexible natural gas.

Figure S6. Materials flow of heavy metals in coal from mining through combustion.

List of Equations:

Equation S1. Trace metal emissions factor

Equation S2. Trace metal mass balance

List of Tables:

Table S1. Comprehensive table of inductively coupled plasma mass spectrometry results of all tested primary pollutant metals.

Table S2. Chemical analysis of the composition of lignite coal from KEK (Korporata Energjetike e Kosovës).

Table S3. ICP-MS trace metal content in Kosovo lignite compared to lignite from other regions

Table S4. Trace metal emissions expressed per final kWh of electricity delivered by country.

Table S5. Annual emissions documented from Kosovo A and B power stations.

APPENDIX:

Methods for trace metal content analysis:



Figure S1. Map of lignite coal mine in Obilic, Kosovo located 12 km from Pristina. Coal samples were taken within a 5-km radius of 42.689° N, 21.069° E. Figure S1 was created using administrative boundaries from European Environment Agency and QGIS.^{1,2}

Mercury: EPA Method 7471A

Cold-Vapor Atomic Absorption Spectroscopy

The sample was first digested with aqua regia. Mercury, a liquid at room temperature, was aerated (evaporated) out of the sample and passed to a cell in an atomic absorption spectrometer. Light is passed through the cell, and the amount of light absorbed is proportional to the amount of mercury in the sample. A mercury lamp is used as the light source, as it produces radiation of the same wavelength at which the mercury atoms in the cell absorb.

Other Metals: EPA Methods 3052 and 6020

HF Digestion and Atomic Emission Spectroscopy

The sample was digested according to Method 3052, where a strong oxidizer, hydrofluoric acid and microwave radiation are used to completely dissolve the sample in water. The solution of metal cations was then analyzed by an Inductively Coupled Plasma Atomic Emission Spectrometer. The solution is injected into argon plasma at greater than 6000 C, atomizing the

sample and exciting the metal ions. When the excited ions return to their unexcited state, they emit light at a unique wavelength and at an intensity proportional to the concentration of that metal in the sample, which is measured by a detector.

In both methods, the instruments were calibrated against metal solutions of known concentration. Reagent blanks, laboratory control samples and spiked samples were used by the laboratory to ensure that no trace metals were lost in the process before detection and that the detection signal was not affected by interferences.

Table S1. Comprehensive table of inductively coupled plasma mass spectrometry results of all tested primary pollutant metals. The unit measure for the results and reporting limit columns is mg/kg.

Analyte	Result	Reporting Limit	Dilution Factor	Batch #	Prepared	Analyzed	Preparation Technique	Analysis Method
<i>Antimony</i>	Not Detected	1.8	100.0	227295	09/17/15	09/18/15	EPA 3052	EPA 6020
<i>Arsenic</i>	9.6	1.6	100.0	227295	09/17/15	09/18/15	EPA 3052	EPA 6020
<i>Beryllium</i>	Not Detected	1.1	100.0	227295	09/17/15	09/18/15	EPA 3052	EPA 6020
<i>Cadmium</i>	Not Detected	0.98	100.0	227295	09/17/15	09/18/15	EPA 3052	EPA 6020
<i>Chromium</i>	19	1.7	100.0	227295	09/17/15	09/18/15	EPA 3052	EPA 6020
<i>Copper</i>	Not Detected	1.1	100.0	227295	09/17/15	09/18/15	EPA 3052	EPA 6020
<i>Lead</i>	Not Detected	1.6	100.0	227295	09/17/15	09/18/15	EPA 3052	EPA 6020
<i>Mercury</i>	0.035	0.020	1.000	227420	09/22/15	09/22/15	METHOD (described above)	EPA 7471A
Nickel	8.5	1.7	100.0	227295	09/17/15	09/18/15	EPA 3052	EPA 6020
Selenium	Not Detected	1.60	100.0	227295	09/17/15	09/21/15	EPA 3052	EPA 6020
Silver	Not Detected	0.98	100.0	227295	09/17/15	09/18/15	EPA 3052	EPA 6020
Thallium	Not Detected	1.2	100.0	227295	09/17/15	09/18/15	EPA 3052	EPA 6020
Zinc	Not Detected	7.8	100.0	227295	09/17/15	09/18/15	EPA 3052	EPA 6020

* Exposure to selenium in addition to arsenic could theoretically mitigate the harmful effects of arsenic because they are antagonistic toxicants, reducing the adverse effects of one another³ However, the presence of selenium in the results we obtained from our inductively coupled plasma mass spectroscopy tests was an analytical error. Selenium should not have been detected in the blank sample, and was recorded in the blank and the sample at the same concentration.

Table S2 contains the chemical analysis reported of the composition of lignite coal as reported by KEK (Korporata Energjetike e Kosovës), the coal mining company and power plant operator in Kosovo.

Table S2. Chemical Analysis of the Composition of Lignite Coal from KEK (Korporata Energjetike e Kosovës).

Coal Content Tested	Quantity	Units
Moisture	38-47	%
Dust	10-14	%
CO _x left over	27-30	%
C-fixed	17-20	%
Volatile matter	25-30	%
Burned matter	40-50	%
Calorific value	7942-9361	kJ/kg
	1700-2239	Kcal/kg
Total sulfur	1-1.1	%
Sulfur in dust	0.5-0.9	%
Sulfur burned	0.06-0.51	%

Table S3 contains the results of ICP-MS trace metal analysis for lignite coal in Kosovo compared to (1) average concentrations of trace metals in a cross section of lignite coal globally (IEA), and (2) trace metal concentrations reported in the literature for lignite coal in the US and China.^{4,5,6}

Table S3. ICP-MS trace metal content in Kosovo lignite compared to lignite from other regions.

All values are in mg metal/kg coal.

Heavy Metal	Content in Kosovo Lignite Coal	International Energy Agency Global Average	Content in coals from China ^{5,6}		Content in coals from USA ⁴		Content in coals around the world ⁴
			Bai et al. (2007)	Dai et al. (2012)	Arithmetic mean	Geometric mean	
Arsenic	9.6 ± 1.6	2.69	4.09	3.79	24	6.5	8.3
Chromium	19 ± 1.7	17.6	16.94	15.4	15	10	16
Mercury	0.035 ± 0.020	0.091	0.154	0.163	0.17	0.10	0.10
Nickel	8.5 ± 1.7	11.1	14.44	13.7	14	9	13

When all units operate, KEK (Korporata Energjetike e Kosovës) manages approximately 30,000 tons of coal per day. According to KEK, the calorific value of lignite in Kosovo ranges from 7942-9361 kJ/kg. The full chemical analysis of lignite from KEK appears in Table S2.

Estimation of trace metal “emissions factor”

Model parameters:

Equation S1:

$$\frac{[\text{TM}]}{\text{kWhe}} = \frac{[\text{TM}] * n_t * n_d * (\text{heat rate}) * C_g}{Q}$$

$\frac{[\text{TM}]}{\text{kWhe}}$ = Trace metal concentration normalized per kWh final electricity delivered (mg/kWhe)

Trace metal concentration = [TM]

Thermal efficiency and heat rate (Btu/kWh)

Q = Calorific value of coal [kJ/kg]

Transmission and distribution network efficiencies = n_t and n_d (%)

Equation S2:

$$M_c = C_c F_c = C_s F_s + C_a F_a + C_g F_g$$

Equation (S2) shows trace metal mass balance. Our model focuses on trace metals in flue gas. The following parameters affect the trace metal partitioning in coal.

M_c = mass of coal

C_c = concentration in coal

C_s = concentration in bottom ash

C_a = concentration in fly ash

C_g = concentration in flue gas

F_c = flow rate in coal

F_s = flow rate in bottom ash

F_a = flow rate in fly ash

F_g = flow rate in flue gas

Results:

Trace metal emission results per final kWh of electricity delivered

Table S4. Trace metal emissions expressed per final kWh of electricity delivered by country.

Trace metal emissions per final unit of electricity delivered [mg/kWh]	Kosovo	Kosovo efficient	China	IEA
[As]	22.3	9.3	6.6	1.1
[Cr]	44.1	18.4	26.9	7.1
[Ni]	19.7	8.2	24.0	4.5
[Hg]	0.08	0.030	0.29	0.03

Table S4 presents the data on metals concentration in mg/kWh_e.

Energy systems model

Our analysis uses four scenarios based on Kittner et al. (2016) for comparison to evaluate premature deaths. The four scenarios are presented below in Figures S2-5. Each scenario details the annual electricity generation supply mix until 2030. They include the business-as-usual generation mix, Euro 2030 path, low-cost solar with natural gas, and low-cost solar without natural gas. The detailed annual kWh generation for each scenario, which has been vetted through stakeholder engagement with civil society and policymakers, are based on the modeling work in Kittner et al. 2016.⁷

Kosovo C is the name of the proposed new coal-fired power plant. In our analysis we assume new coal plants will use best available pollution control technologies. TPP A and B represent the existing Kosovo A and B stations that currently comprise 98% of Kosovo's electricity generation. Zhur is a proposed pumped hydro storage plant included in the Kittner et al. (2016) analysis.

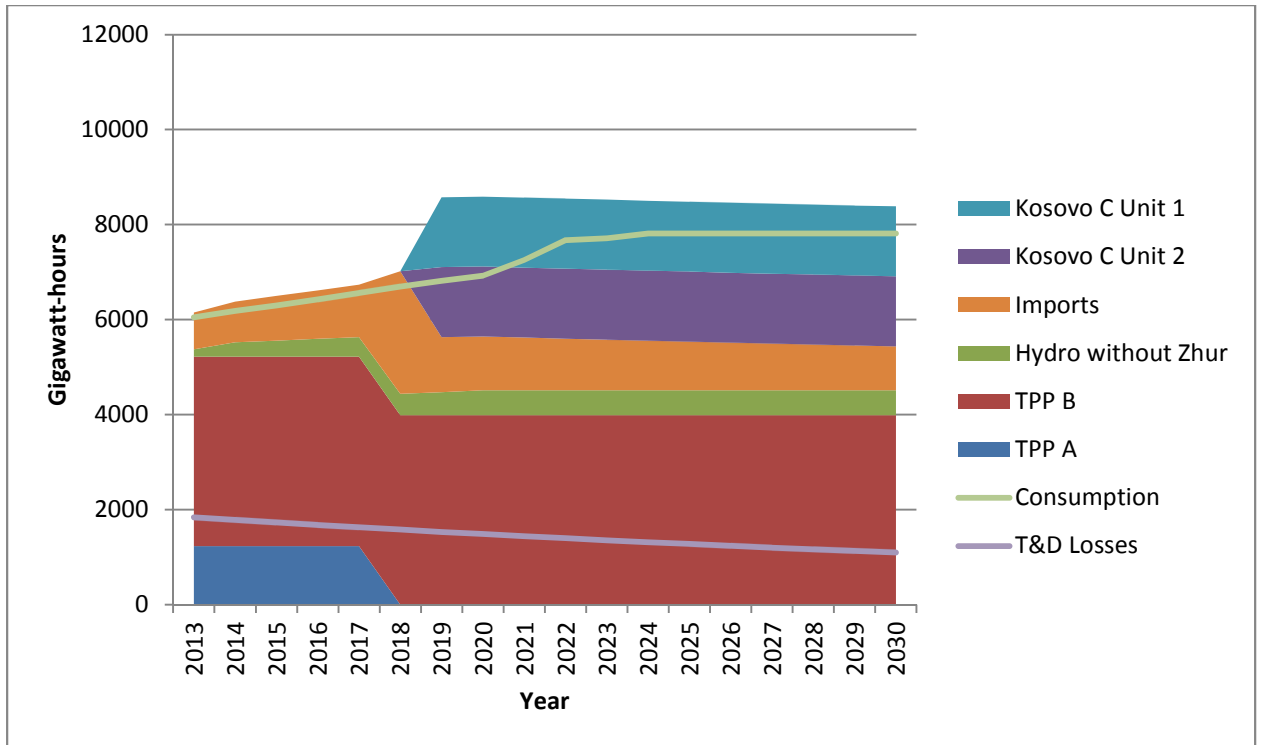


Figure S2. Projected sources of energy generation in a business as usual path that includes the development of Kosovo C.

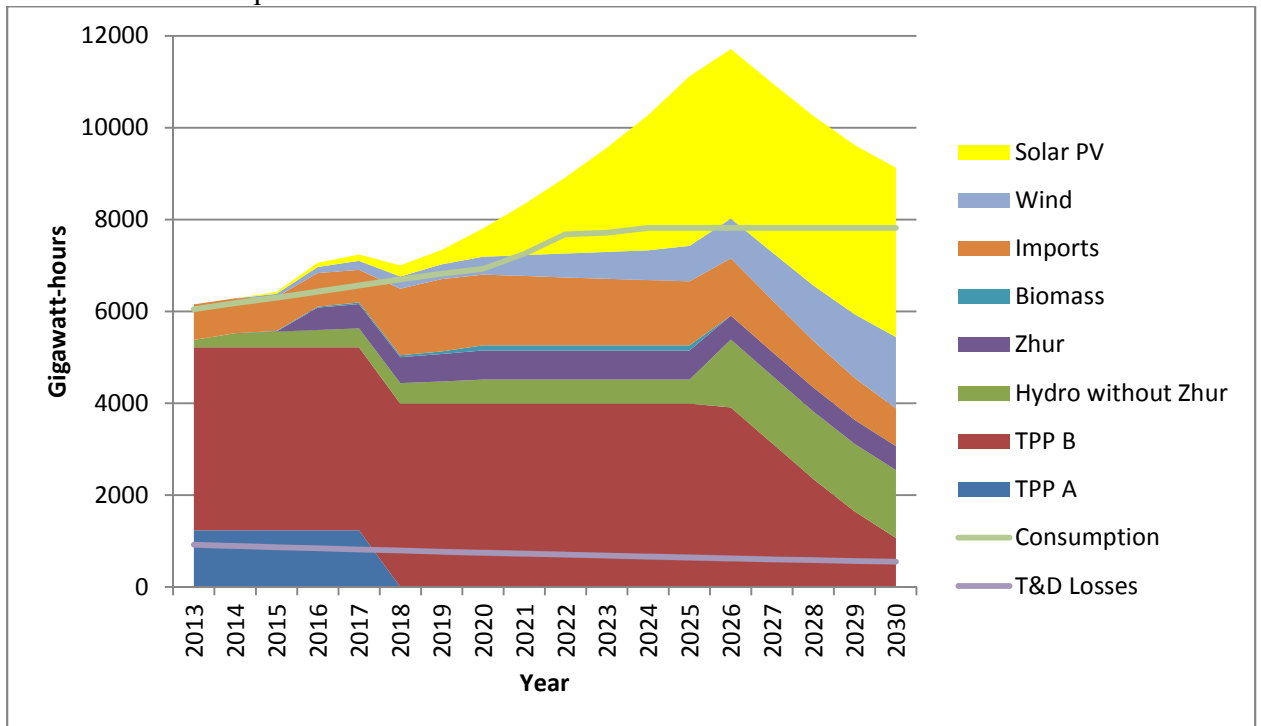


Figure S3. Projected sources of electricity generation in a Euro 2030 path met with energy efficiency measures, 27% CO₂ emission reduction, >27% renewable consumption, expanded power exchange for imports.

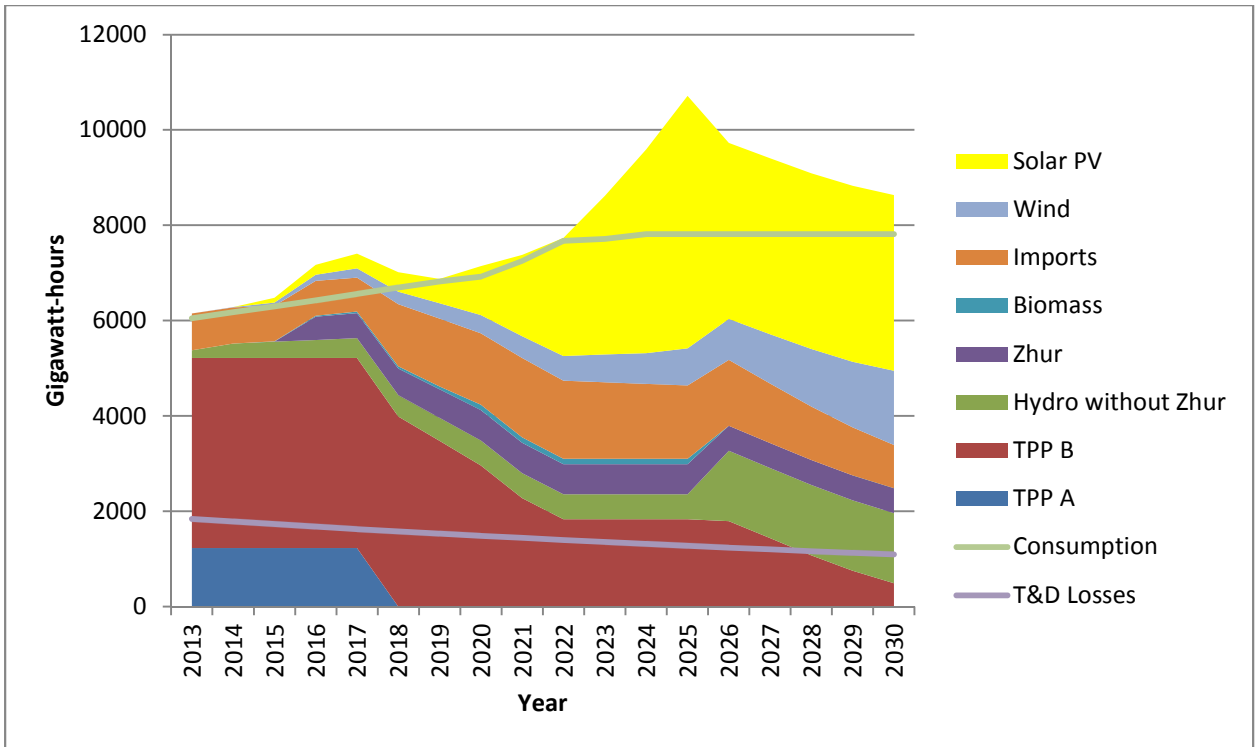


Figure S4. Projected sources of electricity generation in a low-cost solar pathway without flexible natural gas.

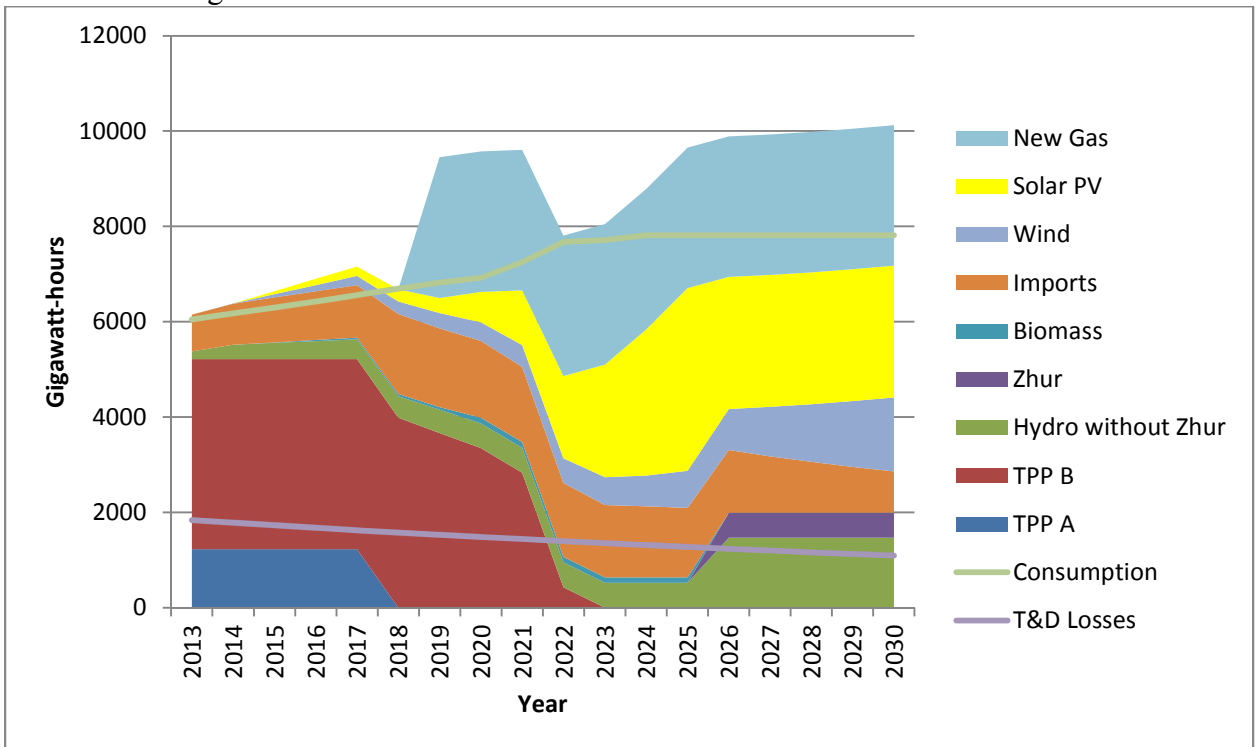


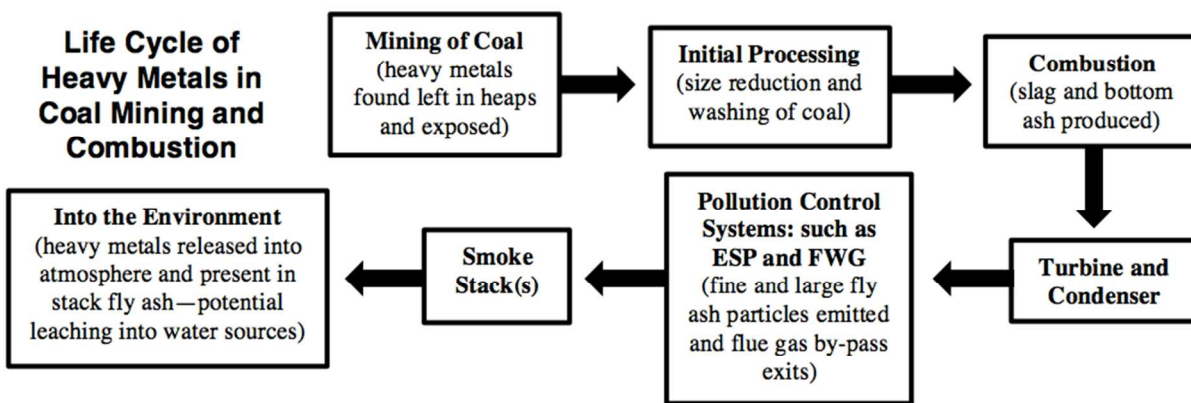
Figure S5. Projected sources of electricity generation in a low-cost solar pathway with flexible natural gas.

Table S5.

Table S5. Annual emissions documented from Kosovo A and B power stations. Source: Ref. (8).

	Annual emissions	European Commission limit
CO₂	5.7 million tons	
SO_x	733 ug/m ³	400 ug/m ³
NO_x	734 ug/m ³	500 ug/m ³
Dust & PM (2010)	1,432 ug/m³	50 ug/m³

Figure S6. Materials flow of heavy metals in coal from mining through combustion.



Exposure to pollutants from lignite coal differs across the life cycle of coal detailed in Figure S6, beginning with mining, through its processing and combustion, and finally with the disposal of fly ash waste. Although exposures could disproportionately affect workers in mining, transportation, and plant operation, their relatively small numbers led us to focus this particular analysis on impacts of coal combustion for surrounding communities.

References:

- (1) European Environment Agency. <https://www.eea.europa.eu/data-and-maps/data/eea-reference-grids-2/gis-files/kosovo-shapefile>
- (2) QGIS Development Team. QGIS Geographic Information System. Open Source Geospatial Foundation Project. <http://qgis.osgeo.org>
- (3) Harte, J.; Holdren, C.; Schneider, R.; Shirley, C. *Toxics A to Z: A guide to everyday pollution hazards*; University of California Press, 1991.
- (4) Nalbandian, H. Trace element emissions from coal. IEA Clean Coal Centre 2012.
- (5) Bai, X.; Li, W.; Chen, Y.; Jiang, Y. The general distributions of trace elements in Chinese coals. *Coal Qual. Technol.* **2007**, 1, 1–4 DOI: 10.1016/j.coal.2011.02.003.

- (6) Dai, S.; Ren, D.; Chou, C.-L.; Finkelman, R. B.; Seredin, V. V.; Zhou, Y. Geochemistry of trace elements in Chinese coals: A review of abundances, genetic types, impacts on human health, and industrial utilization. *Int. J. Coal Geol.* **2012**, 94, 3–21 DOI: 10.1016/j.coal.2011.02.003.
- (7) Kittner, N.; Dimco, H.; Azemi, V.; Tairyán, E.; Kammen, D. M. An analytic framework to assess future electricity options in Kosovo. *Environ. Res. Lett.* **2016**, 11 (10), 104013.
- (8) Dumiak, M. Respiratory health in Kosovo: Europe's new nation and a legacy of coal. *Lancet Respir. Med.* **2017**, 5 (2), 99–100 DOI: 10.1016/S2213-2600(17)30015-2.