

ASSESSMENT OF SOILS POLLUTED WITH HEAVY METALS FROM EMISSIONS EIGHT YEARS AFTER THE DOICEȘTI THERMAL POWER PLANT CLOSURE

Claudia Preda¹, Anca Rovena Lăcătușu¹, A. Vrînceanu¹, Lavinia Burtan¹, Rodica Lazăr¹, Mihaela Lungu¹, M. Dumitru¹, R. Lăcătușu¹

¹National Institute for Soil Science, Agrochemistry and Environment– ICPA Bucharest, Blvd. Mărăști no. 61, Sector 1 Bucharest
E-mail: anca.lacatusu@icpa.ro

Key-words: coal-fired power plant, heavy metals, soil, monitoring

ABSTRACT

Build in 1953 in Dâmbovița County on 40 hectares, the Doicești thermal power plant worked based on combustion of the brown coal extracted from the Șotânga – Filipești mining area. It was developed in multiple stages up to two groups by 200 MW installed in 1979. In 2009, because of the high operating costs and environmental issues, the Doicești thermal power plant has ceased operation. For assessing the effects on the soil in the area influenced by emissions released by thermal power plant exhaust chimneys, a field study was carried out in 2000 year, when soil samples were collected on 0-20 and 20-40cm depths from surveys placed on the cardinal directions, depending on the relief and the dominant winds. Samples have been analyzed to determine their main physico-chemical properties and heavy metals contents. In 2017, after eight years since the thermal power plant has been closed, another field study in the same surveys was carried out, in order to assess the new state of soil quality and heavy metals contents. Data recorded in 2017 as compared with 2000 show a decrease of the Pb, Cd, Co and Ni contents in most surveys, confirming basically that the emissions from the thermal power plant were the main source of soil loading with these heavy metals. Regarding the contents of Zn and Cu, that in normal concentrations are important nutrients for plants, they increased in many surveys after the thermal power plant shutting down, indicate as source of these increases the fertilizers used by landowners.

INTRODUCTION

Coal-fired power plants emit more than 60 different hazardous air pollutants. Also, the coal is the most carbon intensive fossil fuel, emitting 72% more climate changing CO₂ per unit of energy than gas (Keating, M., 2001). Yet, despite billions of dollars of investment, scientists are unable to completely remove harmful emissions from thermal plants (Greenpeace, 2007). Main sources of environment pollution from coal-fired power are fly ash from the smoke stack, bottom ash deposited in ash dumps after the coal is burned, gas released into the air through their chimneys. The coal combustion waste disposed in ash dumps is a risk of toxic metals leaching into nearby surface and ground water. People who drink, over a period of years, an average amount of water contaminated with coal combustion waste have a higher risk of cancer (Schneider, C.G. 2000).

Pollutants from coal-fired power plant emissions could generate severe effects on the environment factors (air, water, soil) and, also, on the nearby population health (Hossain et al., 2015).

Coal-fired power plants produce large quantities of sulphur dioxide (SO₂) and nitrogen oxides (NOX), the key pollutants in the formation of acid rain, which acidifies water bodies, and harms ecosystems. Moreover, SO₂ and NOX contribute to the formation of particulates.

Coal-fired power plants are a major source of suspended particulate matter, nanominerals and ultrafine particles pollution (Kronbauer et al. 2013, Dias et al. 2014). Many scientific studies have shown that raised levels of SPM result in increased illness and premature death from heart and lung disorders, such as asthma and bronchitis (US EPA, 2003). Schneider (2000) found that suspended particulate matter pollution from US power plants cuts short the lives of almost 24,000 people a year. The largest share of suspended particulate matter emissions comes not from direct emissions, but from the conversion of SO₂ and NO_x into fine particle sulphate and nitrate in the atmosphere (Schneider, 2000). Suspended particulate matter gets deposited on the plants which affect photosynthesis. Due to penetration of pollutants inside the plants through leaves and branches, imbalance of minerals, micro and major nutrients in the plants take place which affect the plant growth severely. Spreading and deposition of SPM on soil, disturb the soil strata thereby the fertile and forest land becomes less productive (Pokale, W.K, 2012).

Coal contains numerous persistent, bioaccumulative trace elements that are released during combustion and end up in the atmosphere and water bodies. These include mercury, dioxins, arsenic, radionucleotides, cadmium and lead (Keating, M., 2001). Cadmium inhalation and exposure causes bronchial and pulmonary irritation. A single acute exposure to high levels of cadmium can result in long-lasting impairment of lung function. Cd is considered one of the most probable human carcinogen inductor, the kidney being its major target organ following chronic inhalation and oral exposure. High exposure to chromium VI may result in renal toxicity and internal hemorrhage. Well known as human carcinogen of high potency, chronic effects from exposure to Cr are inflammation of the respiratory tract, effects on the kidneys, liver and gastrointestinal tract.

The Doicești thermal power plant worked based on combustion of the brown coal extracted from the Șotânga – Filipești mining area, an inferior coal which produce large quantities of ash. The ash contributes $\geq 30\%$ of the lignite coal and its main constituents are carbon, alumina, iron, silica, heavy metals, etc. (Sushil et al., 2006, Patel et al., 2016).

Black carbon, the major constituent of air and fly ash particulates, contributes to global warming through absorption of solar irradiance (Ramanathan and Carmichael, 2008), is a good adsorbent having a strong affinity for toxic chemicals, i.e., heavy metals, polycyclic aromatic hydrocarbons (PAHs), dioxins, furans (PCDD/Fs), PCBs, due to its high surface to volume ratio (Ray S. et al., 2012, Hany M. et al., 2014). The BC in soil changes the cyclic process of organic matter and increases cation exchange capacity of soil (Liang B., et al., 2006). The heavy metals in soil affects the quality of food, groundwater, micro-organism activity, and plant growth [Singh J., et al., 2011, Patel et al., 2016).

MATERIALS AND METHODS

Assessment of heavy metals soil pollution by emissions from Doicești coal-fired thermal plant required field investigations and observations on materials constituting the slope lands and terraces surrounding the Doicești power plant. The first field trip for soil sampling was carried out in 2000 when the thermal power plant use to operate at full capacity. The second soil sampling expedition was carried out in 2017, at eight years after the installation closure. Soil samples collected from 27 points at 0-20 cm and 20-40 cm depths, along the cardinal directions, have been subjected to the following determinations: pH potentiometric measurements, using a combined glass – calomel electrode; the total organic carbon content, by Walkley-Black modified by Gogoășă method; the heavy metals (Cu, Zn, Pb, Co, Ni, Mn and Cd) content in hydrochloric solution resulted by solubilization of the residuum obtained after the samples mineralization with perchloric (HClO₄) and nitric (HNO₃) acids mixture, by atomic absorption spectrophotometry, using air-acetylene flame atomization method. All methods are standardized in ISO and STAS systems.

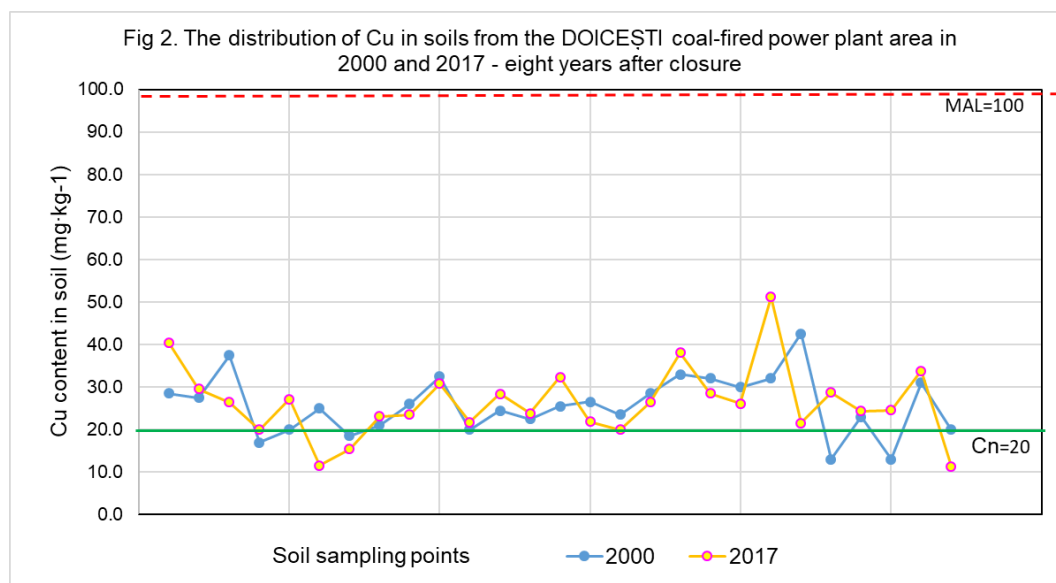
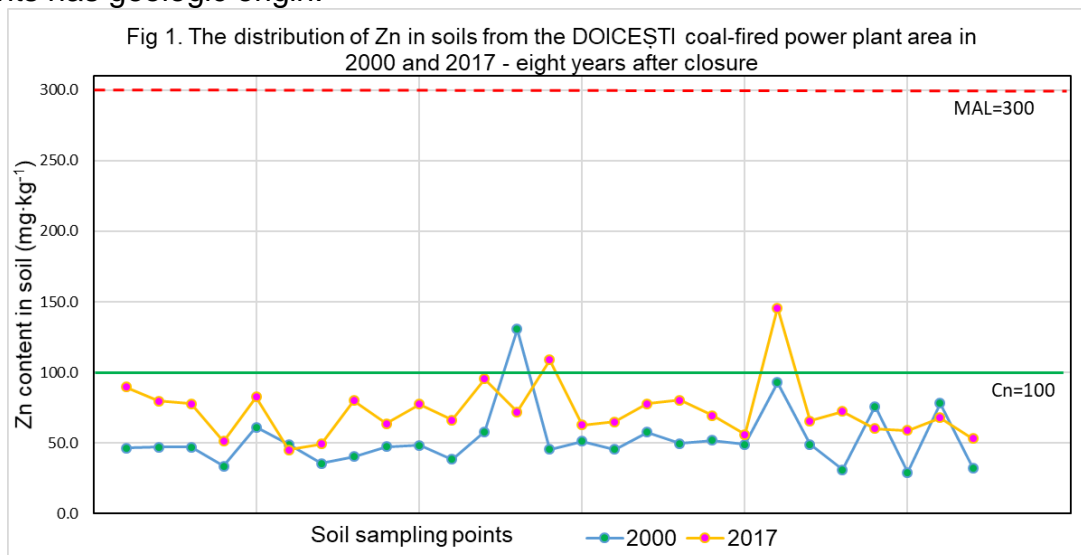
RESULTS AND DISCUSSIONS

Although a broader series of soil analyzes has been made for the assessment of soil pollution as a result of thermal power plant emissions, only the analytical data on heavy metal contents and the comparisons between the values resulting from the two evaluation stages are presented in this paper.

The distribution of heavy metals Zn, Cu, Pb, Co, Ni, Cd in soils from territory influenced by emissions of the Doicești thermal power plant assessed in two different times, in 2000 and 2017 at eight years after the station closure, are illustrated in figures 1-6.

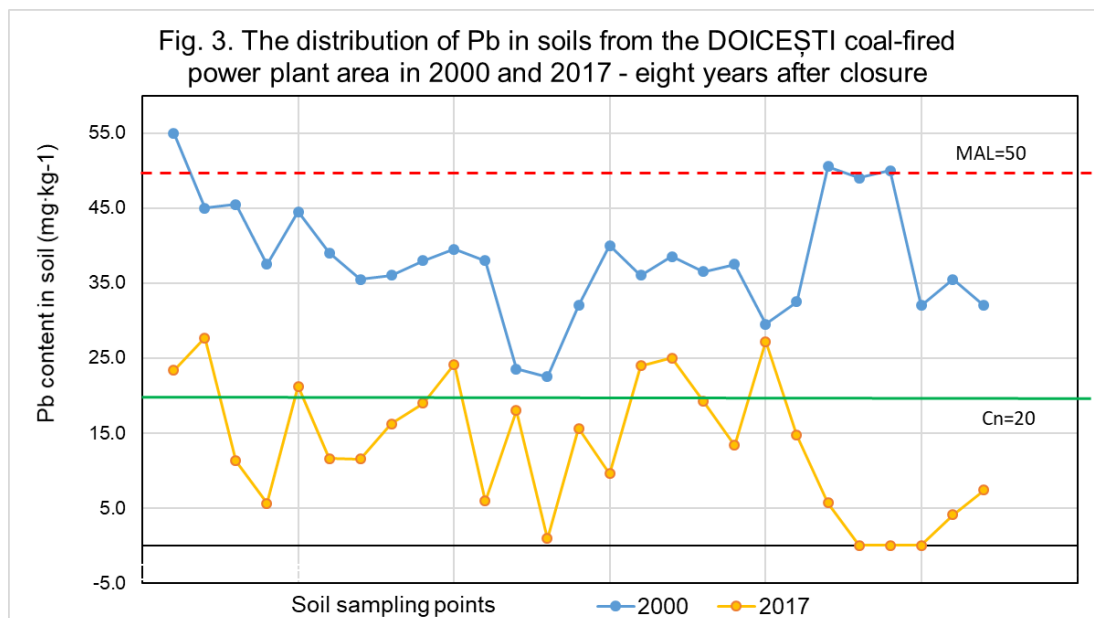
Unexpectedly, the zinc content values reported in 2017 were higher than in 2000, even though they varied within the normal content range in both stages. (Figure 1). Also, for the copper content, more than half values recorded in 2017 were higher than in 2000, although the variation range remained above the normal content limit in both stages (Figure 2).

Should be noted that for none of these metals, Zn and Cu, the values have not reached the maximum admissible limit (MAL) in either investigation stages, which shows that the thermal power plant emissions had at most a minor contribution to the levels of Zn or Cu content in the surrounded soils. Most probable, the main source of these two trace elements has geologic origin.



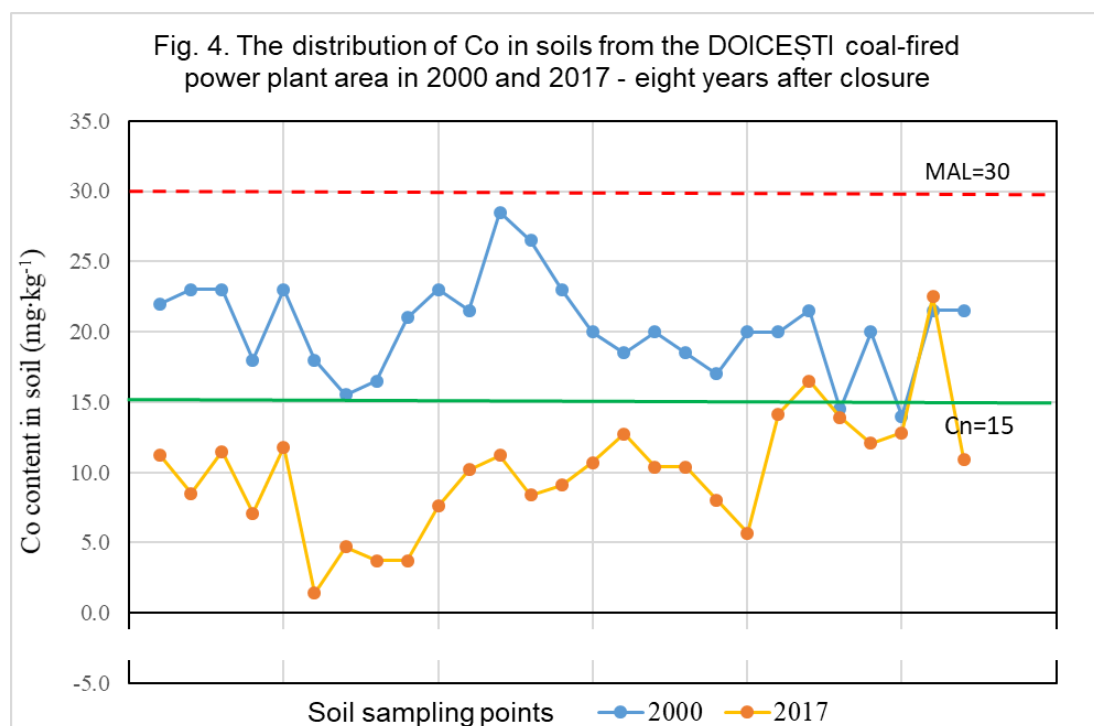
The assessment made in 2017 shows a clear decrease in soil lead content compared to data recorded in 2000 (Figure 3). This time, none of the Pb content values exceed MAL, mostly of the values varied into normal content interval.

Unlike Zn and Cu, in the case of Pb it is obvious that the source of soil pollution was the emissions of the Doicești thermal power plant. At 8 years after the closure of the source, there was also a reduction in the loading degree with Pb of the soils located in its area of influence.



The same situation was recorded with respect to cobalt content. With one exception, after the thermal power plant was closed, the Co content values fall within the variation range of normal soil content (Figure 4).

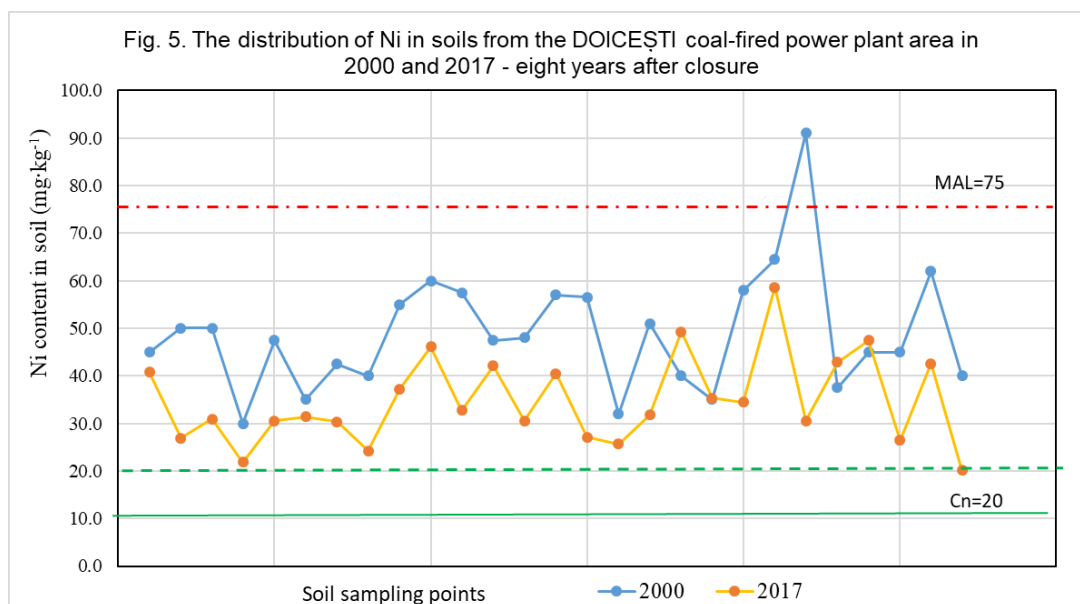
Also, as in the case of Pb, the source of soil pollution with Co was the emissions of the Doicești thermal power plant.



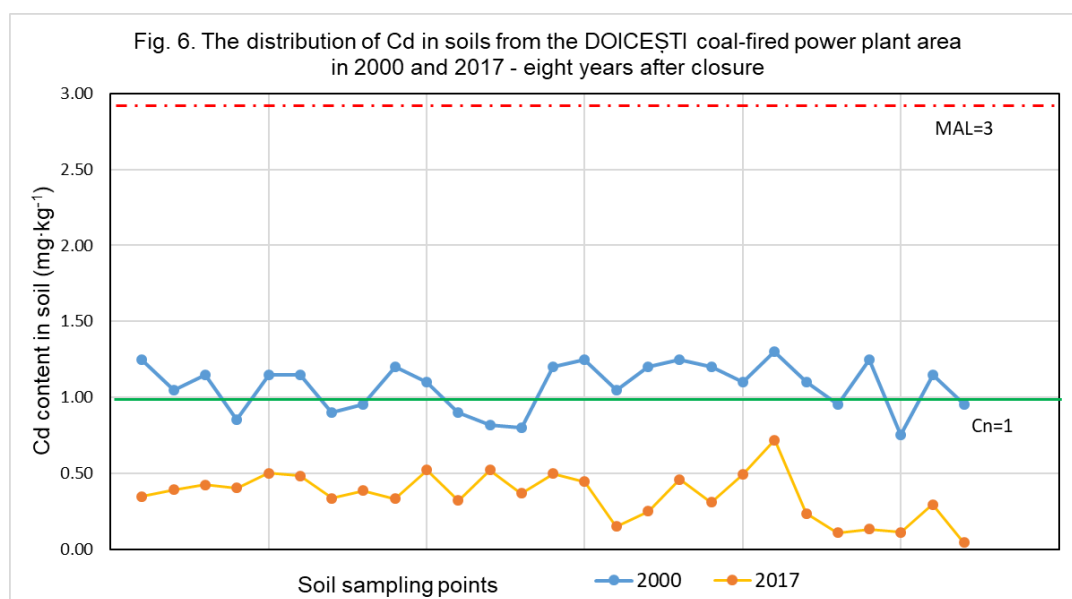
As compared with evaluation made in 2000, in 2017 lower nickel content was recorded in 25 of the 24 monitoring points, although the values were relatively closely to previous registered. The Ni content decrease is not significant, with one exception, the new values exceeding the normal soil content.

Must be noted that in any of the monitoring points the Ni content in soils doesn't rich the MAL.

It could be stated that the thermal power plant emissions caused the pollution with Ni of the soils in surrounding area, but after eight years since the source was shut down the soil loading degree with Ni is still high.



As concerning the cadmium content, it decreased visibly at all monitoring points (Figure 6). If at surveillance made in 2000 only one-third of the monitoring points recorded Cd content values at the upper limit of normal content, the remaining two-thirds exceeding this threshold, in 2017, the mean value calculated for all 27 points was 0.35 mg·kg⁻¹, meaning the lower part of the normal content range in the soil.



Reducing by 67% of the average cadmium content in the investigated territory is a very positive fact because it is one of the heavy metals with high bioaccessibility being considered one of the most toxic, with carcinogenic and teratogenic effects on animals and humans.

CONCLUSIONS

The study to assess the level of soil pollution with heavy metals generated by emissions from the Doicești thermal power plant was carried out in 27 monitoring points, in two stages, in 2000 when the plant was operating at full capacity, and in 2017, 8 years after its closure.

The zinc and copper content values reported in 2017 were higher than in 2000, even though they varied within the normal content range in both stages. However, the average zinc content in 2017 was 38% higher than in 2000, while the average copper content remained about the same.

For both heavy metals the values have not reached the maximum admissible limit in either investigation stages, which shows that the thermal power plant emissions had at most a minor contribution to the levels of Zn or Cu content in the surrounded soils.

The average Pb and Co content decreased by over 50% in 2017 as compared with 2000, and none of the values reached the maximum allowable.

Although the average Ni content decreased by about 29% in 2017, most values exceeded the normal soil content threshold. According to this study, nickel appears to be the most persistent of the heavy metals analyzed.

Heavy metals soil pollution assessment in 2017 recorded the highest average content decreasing, by 67%, for cadmium, most of its values belonging to the lower part of the normal content range in the soil.

As a conclusion of this study it is obvious that the source of soil pollution Pb, Co, Ni and Cd was the emissions of the Doicești thermal power plant, their content significantly decreasing after plant closure.

ACKNOWLEDGMENTS

The work was supported by National Authority for Scientific Research and Innovation by the Project PN 16 07 03 05/2016.

BIBLIOGRAPHY

1. **Dias, C. L., Oliveira, M. L., Hower, J. C., Taffarel, S. R., Kautzmann, R. M., & Silva, L. F.**, 2014. Nanominerals and ultrafine particles from coal fires from Santa Catarina, South Brazil. *International Journal of Coal Geology*, 122, 50–60.
2. **Hany M., Bandowe B.A.M., Wei C., Cao J.J., Wilcke W., Wang G.H., Ni H.Y., Jin Z.D., An Z.S., Yan B.Z.**, 2014. Stronger association of polycyclic aromatic hydrocarbons with soot than with char in soils and sediments. *Chemosphere* 119, 1335, 2014
3. **Hossain, M.N., Paul, S.K. & Hasan, M.M.** 2015. Environmental impacts of coal mine and thermal power plant to the surroundings of Barapukuria, Dinajpur, Bangladesh, *Environ Monit Assess* (2015) 187: 202. <https://doi.org/10.1007/s10661-015-4435-4>
4. **Keating, M.**, 2001. Cradle to the Grave: The Environmental Impacts from Coal, www.catf.us/publications/reports/Cradle_to_Grave.pdf
5. **Kronbauer, M. A., Izquierdo, M., Dai, S., Waanders, F. B., Wagner, N. J., Mastalerz, M.**, 2013. Geochemistry of ultra-fine and nano-compounds in coal gasification ashes: a synoptic view. *Science of the Total Environment*, 456, 95–103.
6. **Liang B., Lehmann J., Solomon D., Kinyangi J., Grossman J., Oneill B., Skjemstad J.O., Thies J., Luizao F.J., Petersen J., Neves E.G.**, 2006. Black carbon

- increases cation exchange capacity in soils. *Soil Science Society of America Journal* 70 (5), 1719, 2006.
7. **Patel S.K., R. Sharma, N. S. Dahariya, R. K. Patel, B. Blazhev, L. Matini.** 2016. Black Carbon and Heavy Metal Contamination of Soil, *Pol. J. Environ. Stud.* Vol. 25, No. 2 (2016), 717-724
 8. **Pokale, W.K.**, 2012. Effects of thermal power plant on environment, *Sci. Revs. Chem. Commun.:* 2(3), 2012, 212-215
 9. **Ramanathan V., Carmichael G.** 2008. Global and regional climate changes due to black carbon. *Nature Geoscience* 1, 221, 2008.
 10. **Ray S., Khillare P.S., Kim K.H., Brown R.J.,** 2012. Distribution, sources, and association of polycyclic aromatic hydrocarbons, black carbon, and total organic carbon in size-segregated soil samples along a background-urban-rural transect. *Environmental Engineering Science* 29 (11), 1008, 2012.
 11. **Schneider, C.G.** , 2000. Death, Disease and Dirty Power: Mortality and Health Damage Due to Air Pollution from Power Plants, Clean Air Task Force, www.catf.us/publications/reports/Dirty_Air_Dirty_Power.pdf
 12. **Singh J., Kalamdhad A.S.,** 2011. Effects of heavy metals on soil, plants, human health and aquatic life. *International Journal of Research in Chemistry and Environment* 1 (2), 15, 2011.
 13. **Sushil S., Batra V.S.** Analysis of fly ash heavy metal content and disposal in three thermal power plants in India. *Fuel* 85 (17-18), 2676, 2006.
 14. *****Greenpeace report,** 2007. The Environmental Impacts of Coal. Available at <http://www.greenpeace.org/new-zealand/Global/new-zealand/report/2007/1/enviro-impacts-of-coal.pdf>
 15. *****US EPA,** 2003. Effects of Acid Rain: Human Health, www.epa.gov/airmarkets/acidrain/effects/health.html, viewed 9/12/04.