Health Risk Calculator of Toxic Pollutants in Black Sea Basin

Because the contamination of environmental compartments (water, soil, biota) with heavy metals, radionuclides, hydrocarbons, detergents or pharmaceuticals or release of radioactive gases (radon, thoron) can cause health problems, we considered that it was necessary to create a computer application for the detection of health risks. This platform will take into account each pollutant group, the location in water, soil, flora or fauna and the age group of persons (children, adults or seniors).

In order to create the application (Fig. 1), we used a series of indices existing in the literature and measured or historical data.

Fig. 1. Health risk calculator version 1.0

Review no.1. of literature health risk indices

Single pollution index (SPI) and Nemerow composite pollution index (NCPI) is used to classify the soils in terms of heavy metals pollution.

The bioaccumulation factor (BAF) is used to quantify the transfer of heavy metals from soil to plants.

Chronic daily intake (CDI, mg/kg/day) refers to three indexes used to evaluate exposure to havy metals in the soil by ingestion, inhalation, and dermal touch. Hazard index (HI) estimates the combined risk for non-carcinogenic effects, while TCR index estimates the carcinogenic risk (Hu et al, 2017, Huang et al, 2019, Koki et al 2015, Majlesi et al, 2018). The equation

$$ILCR = CDI \times CSF$$

is used for the calculation of the cancer risk (the cancer slope factor CSF is the risk generated by the amount of one mg/kg/day of carcinogen chemical during the entire lifetime) (Mohammadi et al, 2019, Alidadi et al, 2019).

The literature proposes formulas to calculate the estimated daily intake (EDI) and estimated short-term intake (ESTI) of pesticide residues and (Lozowicka et al, 2013).

In (Wilson et al, 2015) is proposed the following equation to calculate cancer risk after polycyclic aromatic hydrocarbons (PAHs) exposure (calculated through *BaPeq*) after a 78-year life span (28,470 days) due to sea food ingestion:

Risk = {[(mg BaPeq/kg shrimp) × (kg shrimp consumed/day) × (365 days/year) × years exposed]÷ (kg body weight × 28,470 days)} × oral slope factor.

The BaPeq is calculated based on toxic equivalency factors of individual PAHs (TEFs).

Soil contamination with PAHs (Thiombane et al., 2019)

Several PAH species including benzo(a)pyrene (as most carcinogenic compound) have been classified into probable (2A) or possible (2B) human carcinogens by the International Agency for Research on Cancer. BaP is a five ring (C_20H_{12}) compound, which is mutagenic for human cells in culture (and carcinogenic in whole animal assay. According to the literature, the toxic equivalent factor for BaP is one (1), which is highest among all the PAHs. One approach in estimating the carcinogenic potency associated with the exposure of a given PAH compound can be obtained by calculating its **BaPeq for each individual PAH species**. In order to calculate the carcinogenic potencies associated with the total PAH exposures from soil we pragmatically used the sum of each individual BaPeq (i.e., total-BaPeq) as a *surrogate indicator*. Therefore, in the present project, toxic equivalent factor (TEF) of the given species relative to BaP carcinogenic potency will be used.

For soil contamination with PAHs, the TEFs are presented in the Table 1 (Masih and Taneja, 2006).

Table 1. TEFs of PAHs with BAP exposure

PAHs	**TEFs**	**PAHs**	**TEFs**
NAP	0.001	B(a)A	0.1
ACY	0.001	CHR	0.01
ACE + FLU	0.001	B(b)F	0.1
PHE	0.001	B(k)F	0.1
ANT	0.01	B(a)P	1
FLT	0.001	B(ghi)P	0.01
PYR	0.001	**Total**	**1.33**

NAP—Naphthalene, ACY—Acenapthylene, ACE—Acenapthene, FLU—Fluorene, PHE—Phenanthrene, ANT—Anthracene, FLT—Fluoranthene, PYR—pyrene, B(a)A—Benzo(a)fluoranthene, CHY—Chrysene, B(b)F—Benzo(b)fluoranthene, B(k)F—Benzo(k)fluoranthene, B(a)P—Benzo(a)pyrene, B(ghi)P—Benzo(ghi)perylene.

Other indices potential to be used in the health risk assessment (Yi et al, 2017):

1. Tolerabile daily intake

   EDI – estimated daily intake depends on the metal concentration, food consumption and body weight.

   In order to evaluate the risk of consumption HM from fish consumption, it was considered that the dose was equal to the absorbed pollutant dose, meaning that cooking had no effect on the pollutants; the average body weight of China people is 55.9 kg; people that are living on the coast are eating 105 g fish and crayfish per day.

   $$EDI(for\ adults) = \frac{C \times C_{cons}}{B_w}$$

   C- concentration HM in fish (mg/kg) wet weight

   C_{cons}- the average daily consumption of fish

   B_w- body weight

2. The carcinogenic risk is the ratio of the exposure dose to the reference dose (RfD) and represents the risk of noncarcinogenic effects. If it is less than 1 the exposure level is less than the RfD. This indicates that the daily exposure at this level is unlikely to cause adverse effects during a person's lifetime, and vice-versa. The Doses were calculated using standards assumptions from the integrated USEPA (2000) risk analysis.

   $$THQ = \frac{EF_r \times ED_{tot} \times FIR \times C}{R_f D_O \times B_w \times AT_n} \cdot 10^{-3}$$

   where:

   EF_r –exposure frecvency (350 days/year)

   ED_{tot}- exposure duration (30 years)

   FIR- food ingestion rate (g/day)

   10^{-3}- unit conversion factor

   C– HM concentration in fish (mg/kg, wet weight)

   $R_f D_o$- is the oral $R_f D$ (mg/ kg day)

   B_w- body weight

   AT_n- average exposure time for noncarcinogens 365 day/ year x number of exposure years assuming 30 years.

   THQ_{total}- here was the arithmetic sum of the individual metal THQ values

3. Pollution intensity (ΔI_X) represents the changes of measured concentrations of heavy metals (HM) that was calculated as pollution intensity. The accumulative ecological risc of HM was calculated as follows:

   $$\Delta I_X = \frac{|I_{1x} - I_{ox}|}{max(I_{1x} \cdot I_{ox})}$$

   Where:

   x- is the studied indicator

   I_{0x} is the standard concentration

   I_{1x} is the detected concentration in fish or sediment

4. The eco-impact (e_{io}) was employed to integrate the environment mental pollution probability P_x, pollution intensity (ΔI_X) and relative vulnerability (V_i) and can be calculated as the following equation to quantify the accumulative ecological risks of metals.
   $e_{io} = \Delta I_X \times P_x \times V_{ix}$
   where
   e_{io} is found to be between 0 and 1
   V_{ix}, P_x and V_i were obtained from historical data

5. Bioconcentration
   $BCF = \frac{C_{biota}}{C_{water}}$

6. Human risk assessment by estimating daily intake
   $EDI = \frac{(C \times IR_d)}{Bw}$

7. The non-carcinogenic risk
   $THQ_{non-carcinogenic} = \frac{(EF \times ED \times IRd \times C)}{(Rfd \times Bw \times AT)}$

Water radionuclides **(Pintilie et al., 2016)**

The annual equivalent effective dose due to water ingestion

The specific activities of the natural radionuclides from drinking water are mainly due to the presence of naturally occuring radionuclides of both the uranium and thorium decay series. In order to calculate the annual internal dose, the values of effective dose conversion factor by ingestion, CF (in Sv Bq^{-1}) could be used, presented in Table 2.

Table 2. Effective dose conversion factors by ingestion, CF (Sv Bq^{-1}), for the most important natural radionuclides.

Radionuclide	Half life	Adults CF (Sv Bq^{-1})
^{238}U	4.47E+09 y	4.5E-08
^{235}U	7.04E+08 y	4.7E-08
^{234}U	244000 y	4.9E-08
^{224}Ra	3.66 d	6.5E-08
^{226}Ra	1600 y	2.8E-07
^{210}Pb	22.3 y	6.9E-07
^{228}Ra	5.75 y	6.9E-07
^{210}Po	138 d	1.2E-06
^{40}K	1.28E+09 y	6.2E-09

For the most important natural radionuclides from uranium and thorium series, the effective dose conversion by ingestion for adults grows in the following order:

$$^{238}U < ^{235}U < ^{234}U < ^{224}Ra < ^{226}Ra < ^{210}Pb < ^{228}Ra < ^{210}Po$$

Therefore, in order to calculate the annual internal dose, we considered that alpha gross activity is due to ^{226}Ra and ^{210}Po and beta gross activity due to ^{228}Ra and ^{210}Pb, which are emitters with the highest effective conversion factors CF.

The annual effective dose equivalent D_{ef} (Sv y^{-1}) associated with radiation exposure **through the ingestion of water** was estimated to assess the health risk for adults using the equation:

$$D_{ef} = \Lambda_{\alpha/\beta} \times IR_w \times CF$$

where $\Lambda_{\alpha/\beta}$ is gross alpha/beta activity (Bq L^{-1}); IR_w – intake of water for one person in one year (L y^{-1}); CF – age-dependent effective dose conversion factor (Sv Bq^{-1}). For example, for adult people, the annual consumption rate (IR_w) is estimated at the value of 730 L, according to WHO (age >17 years).

Soil and sediment radionuclides **(Ene, 2019; Ene et al., 2019a,b)**

1. Absorbed gamma dose rate (D)

The external gamma absorbed dose rate due to terrestrial γ-rays in the air at 1m above ground level is calculated from the measured activities of 226Ra, 232Th and 40K in the soil, sand and sediment samples. The calculations are performed according to the following equation

$$D = 0.462\ C_{Ra} + 0.604\ C_{Th} + 0.042\ C_K$$

where D is the dose rate in mGy/h. About 99% of the external gamma dose rate from the 238U series was delivered by the 226Ra subseries. So, disequilibrium between 226Ra and 238U will not affect the dose estimation from the measurement of 236 Ra. In the above equation it is asumed that all decay product of 226Ra and 232Th are in radioactive equilibrium with precursors.

2. External hazad index H_{ex}

The external hazard index in a evaluation of the hazard of the natural gamma radiation. This index is used to assess die radiological suitability of a material. The prime objective of this index is to limit the radiation dose to the admissible dose equivalent limit of 1 mSv/y and can be evaluated using the following equation

$$H_{ex} = C_{Ra}/370 + C_{Th}/259 + C_K/4810$$

The value of H_{ex} must be lower than to unity in order to keep the radiation hazard insignificant. If H_{ex} > 1 implies that activities involving the use of materials are safe and do not attract any high levels of radiation exposure.

Bibliography

1. Alidadi H., Sany S. B. T., Oftadeh B. Z. G., Mohamad T., Shamszade H., and Fakhari M., 2019, Health risk assessments of arsenic and toxic heavy metal exposure in drinking water in northeast Iran, Environmental Health and Preventive Medicine, vol. 24, Article number: 59.
2. Brito, M.G., Costa, C., Vendas, D., and Serranheira, F., 2015, Soil contamination and human health risk assessment at a former industrial site in a densely populated urban area, MIST 2015 (Modelling Innovation, Sustainabilityand Technology), Conference proceedings.
3. Ene A., Adrian Cîrciumaru, Iulian Gabriel Bîrsan, Elena Zubcov, Oleg Bogdevich, Thomas Spanos, Viorel Cartaș, Eugenia Pascu, Violeta Pintilie, Florin Sloată, Nicusor-Daniel Patrascu, Liviu Vodarici, Mădălina Stăvărache, 2019a, "Radioactivity Levels in Selected Areas of the Black Sea Basin in Romania, Republic of Moldova and Greece", S1.08, Abstract book MONITOX International Symposium "Deltas and Wetlands" September 15-17 2019, Tulcea, Romania, p.26.
4. Ene A., Pintilie V., Pantelica A., 2019b, Assessment of radon, thoron and their descendants in selected indoor environments in Romania, International Symposium on Natural Radiation Sources – Challenges, Approaches and Opportunities, 21-24 May 2019, Bucharest, Romania
5. Ene A., 2019, Clase de substanțe toxice investigate în cadrul proiectului MONITOX. Izotopi radioactivi și nivelul dozelor de radiații nucleare în regiunea Dunării de Jos și Bazinului Mării Negre / Classes of toxic substances investigated in the frame of MONITOX project. Radioactive isotopes and level of nuclear radiation doses in Lower Danube region and Black Sea Basin, Regional Workshop „Environmental Pollution of Aquatic Ecosystems of Danube-Black Sea Basin" , Chisinau, 16-17 May 2019.
6. Hu B., Jia X., Hu J., Xu D., Xia F., and Li Y., 2017, Assessment of Heavy Metal Pollution and Health Risks in the Soil-Plant-Human System in the Yangtze River Delta, China, International Journal of Environmental Research and Public Health, 14(9), 1042; https://doi.org/10.3390/ijerph14091042.
7. Huang S., Shao G., Wang L., Wang L., and Tang L., 2019, Distribution and Health Risk Assessment of Trace Metals in Soils in the Golden Triangle of Southern Fujian Province, China, International Journal of Environmental Research and Public Health, *16*(1), 97; https://doi.org/10.3390/ijerph16010097.
8. Jiang X., Lu W.X., Zhao H. Q., Yang Q. C., and Yang Z. P., 2014, Potential ecological risk assessment and prediction of soil heavy-metal pollution around coal gangue dump, Natural Hazards and Earth Syste, Sciences, 14, 1599–1610, doi: 10.5194/nhess-14-1599-2014.
9. Koki I.B., Bayero A. S., Umar A., and Yusuf S., 2015, Health risk assessment of heavy metals in water, air, soil and fish, African Journal of Pure and Applied Chemistry, vol. 9(11), pp. 204-210, doi: 10.5897/AJPAC2015.0654.
10. Lewis M. A., 1990, Chronic toxicities of surfactants and detergent builders to algae: A review and risk assessment, Ecotoxicology and Environmental Safety vol. 20, issue 2, 123-140, https://doi.org/10.1016/0147-6513(90)90052-7.
11. Łozowicka B., Kaczyński P., Rutkowska E., Jankowska M., and Hrynko I., 2013, Evaluation of pesticide residues in fruit from Poland and health risk assessment, Agricultural Sciences, vol.4, no.5B, 106-111, doi:10.4236/as.2013.45B020.
12. Majlesi M., Pashangeh S., Salehi S. O., and Berizi E., 2018, Human Health Risks from Heavy Metals in Fish of a Fresh Water River in Iran, International Journal of Nutrition Sciences, vol. 3(3), 157-163.
13. Masih A., Taneja A., 2006, Polycyclic aromatic hydrocarbons (PAHs) concentrations and related carcinogenic potencies in soil at a semi-arid region of India, Chemosphere, vol. 65, 449–456
14. Mohammadi A. A., Zarei A., Majidi S., Ghaderpoury A., Hashempour Y., Saghi M. H., Alinejad A., Yousefi M., Hosseingholizadeh N., and Ghaderpoori M., 2019, Carcinogenic and non-carcinogenic health risk assessment of heavy metals in drinking water of Khorramabad, Iran, MethodsX, Vol. 6, 1642-1651, doi: 10.1016/j.mex.2019.07.017.
15. Pintilie, V., Ene, A., Georgescu, L.P., Moraru, L., Iticescu, C., 2016, Measurements of gross alpha and beta activity in drinking water from Galati region, Romania, Romanian Reports in Physics 68 (3), 1208–1220.
16. Thiombane M., Albanese S., Di Bonito M., Lima A., Zuzolo D., Rolandi R., Qi S., De Vivo B., Source patterns and contamination level of polycyclic aromatic hydrocarbons (PAHs) in urban and rural areas of Southern Italian soils, 2019, Environ Geochem Health, 41(2), 507-528
17. Wilson M. J., Frickel S., Nguyen D., Bui T., Echsner S., Simon B. R., Howard J. L., Miller K., and Wickliffe J. K., 2015, A Targeted Health Risk Assessment Following the Deepwater Horizon Oil Spill: Polycyclic Aromatic Hydrocarbon Exposure in Vietnamese-American Shrimp Consumers, Environmental Health Perspectives, vol. 123, no. 2, http://dx.doi.org/10.1289/ehp.1408684.
18. Yi Y., Tang C., Yi T., Yang Z., Zhang S., 2017, Health risk assessment of heavy metals in fish and accumulation patterns in food web in the upper Yangtze River, China, Ecotoxicology and Environmental Safety, vol. 145, p. 295-302.