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Towards integrating toxicity characterization into environmental studies: case study of bromine in soils

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Pollution from bromine and some of its related compounds is currently unregulated in soil from Russia and other countries, and tools for sound assessment of environmental impacts of bromine contamination are largely missing. Hence, assessing potential implications for humans and ecosystems of bromine soil contamination is urgently needed, which requires the combination of measured soil concentrations from environmental studies and quantified potential toxicity impacts. To address this need, we used data from an experimental study assessing bromine in soils (384 samples) of Tomsk oblast, Russia, starting from measured concentrations obtained by Instrumental Neutron Activation Analysis in an earlier study. From these data, we calculated the bromine mass in soils and used these as starting point to characterize related cumulative impacts on human health and ecosystems in the Tomsk region, using a global scientific consensus model for screening-level comparative toxicity characterization of chemical emissions. Results show that the combination of sampling methodology with toxicity characterization techniques presents a new approach to be used in environmental studies aimed at environmental assessment and analysis of a territory. Our results indicate that it is important to account for substance-specific chemical reaction pathways and transfer processes, as well as to consider region-specific environmental characteristics. Our approach will help complement environmental assessment results with environmental sustainability elements, to consider potential tradeoffs in impacts, related to soil pollution, in support of improved emission and pollution reduction strategies.

Keywords Bromine contamination · Tomsk oblast · Characterization factors · USEtox · Human toxicity · Freshwater ecotoxicity

Introduction

Bromine (Br), a chemical element belonging to the group of halogens, has the atomic number of 35. Br is a typical trace element and its major sources are mostly natural: seawater, salt lakes and lake brines, highly mineralized reservoir waters, and the waters of oil deposits (Vinogradov 1939; Chemical Encyclopedia 1988; Emsley 1989). However, bromine

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contamination could appear due to human activities as far as bromine and its compounds are used in numerous areas such as chemical and food industries, medicine, pharmaceutics, agriculture, and nuclear industry (Filov 1988; Greenwood and Ershno 2008; Yoffe et al. 2013). If not specified otherwise, we use the term "bromine" to refer to the element in its various forms including related compounds.

Bromine is considered as one of the essential elements (McCall et al. 2014). However, there is considerable data indicating its toxic effects. Since bromine can be emitted to the environment in the form of different ions or compounds, related toxic effects could vary significantly from one compound/form to another. The literature data on toxicity presented hereafter describe the toxicity of bromide (Br^-) that is the anion of the element bromine (Br_2). In some cases, bromide could provoke phytotoxicity, since it could replace chlorine and affect changes in cell membrane permeability (Nazer et al. 1982; Kabata-Pendias 2010). Likewise, animal studies describe bromide as toxic at varying dose levels (van Leeuwen et al. 1983; World Health Organization 1988; IUCLID 2000).

With respect to effects on human health, bromine is reported to play an important role in the appearance and development of various diseases (Valdés et al. 2012). Elevated bromine contents have been found in the heart tissue of patients suffering from uremia (Pehrsson and Lins 1983), dilated cardiomyopathy (Bumbalova et al. 1991), and sickle-cell anemia, and also in cancerous breast tissue and in the brain of patients with Alzheimer's disease (Ehmann and Vance 1996), and others.

The widespread use of bromine today and the potential danger caused by anthropogenic entry of the element and its compounds into the environment, as well as its negative impact on living organisms, determine the existence of the regulatory standards in some countries. For example, in Russia, elemental bromine and its several compounds are standardized (i.e., maximum permissible concentrations are set) in workplaces air (GN 2.2.5.1313-03 2003) and ambient air in public areas (GN 2.1.6.1338-03 2003). According to these standards, bromine presents a class II danger, i.e., is highly dangerous. There are also established hygienic standards for bromide in water in Russia (GN 2.1.5.1315-03 2003). There are no limit values for bromide in water, established by the WHO, according to which "it occurs in drinking water at concentrations well below those of health concern" (World Health Organization 2011), but some recommendation values are proposed as an alternative (World Health Organization 2009). However, today, there is a significant gap in the establishment of standards or recommendations for bromine levels in soils.

Studies show that the content of bromine in soils usually ranges from 5 to 40 mg/kg (Kabata-Pendias 2010); according to Vinogradov (1957), the average content is 5 mg/kg. In accordance with the electronic structure of the bromine atom, the element in soils can be found in the form of various ions: Br^- (the most widespread form), BrO^-, $BrO3^-$, $BrO4^-$, as well as organic compounds (Konarbaeva 2008). A major contribution to studying Br in soils was made by Vinogradov (1957), Yamada (1968), Yuita (1983), Yuita et al. (1982), Konarbaeva (2008), and Kabata-Pendias (2010).

In the present paper, the area of interest is Tomsk oblast, an administrative region of the Russian Federation, where chemical and oil industries, together with agriculture, are among the main contributors to chemical pollution of soils (Banks et al. 2000; Zhornyak et al. 2016). A recent study (Perminova et al. 2017) showed that among 26 chemicals identified in the soils of Tomsk oblast, bromine concentrations are significantly higher compared with background soil concentrations from local park areas and levels found in soils of other regions of Russia. However, the mechanisms behind bromine contamination in soils of Tomsk oblast, along with the associated impacts on human and environmental health, are still largely unclear.

In response, we propose to use a modeling approach helping to determine current bromine soil contamination patterns in Tomsk oblast and to screen potential related negative impacts on humans and the environment in order to better understand and mitigate bromine-related emissions and impacts. Measured bromine concentrations in our case are not bromine emitted itself, but the total possible bromine found in soils in different forms. Since bromine could originate from different sources in various forms or/and being presented as a compound, it is important to account for the correct emission forms that will ultimately be present in the environment. However, there is currently no screening-level modeling framework available for assessing the fate and exposure of inorganic substances that are not metal ions (Kirchhübel and Fantke, 2019). To demonstrate this issue, we are testing in the present study different modeling assumptions in a global scientific consensus model for screening-level characterization of fate, exposure, and effects of chemical emissions (Rosenbaum et al. 2008; Henderson et al. 2011). More specifically, we will model bromine compound emissions on the one hand in the same way as metal ions are modeled, and on the other hand in the same way as organic substances are modeled. This allows us to contrast the different assumptions and provide some input for developing new methods for consistently assessing fate, exposure, and effects of inorganic substances other than metal ions.

Quantifying life cycle toxicity impacts based on existing actual pollutant levels in soil will, in addition, be useful in complementing pollutant threshold levels by uncovering potential tradeoffs between different multi-media fates and multi-pathway exposures, related to soil contaminants contributing to potentially negative impacts on humans and the environment (Fantke et al. 2018a, 2018b). In the present study, we focus on the following three objectives: (1) to determine the cumulative mass of bromine in soil in the different districts of Tomsk oblast and discuss potential sources; (2) to characterize cumulative human toxicity and ecotoxicity impact potentials of bromine mass in soils of Tomsk oblast; and (3) to identify existing challenges of combining environmental studies with screening-level toxicity characterization, and to discuss future research needs as input to develop operational methods for mitigating contamination from emissions of inorganic substances.

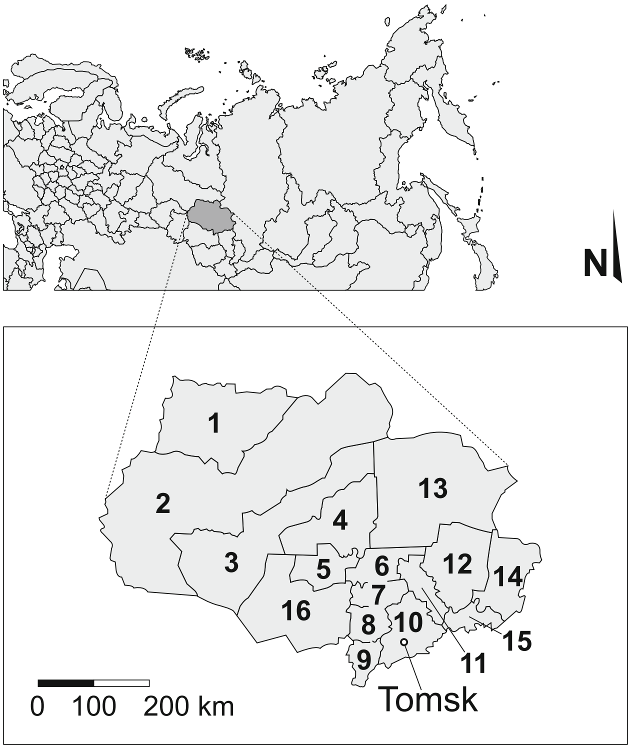
Methodology

Study area

Tomsk oblast is a region of the Russian Federation situated in the south-eastern part of the largest plain in the world—the West Siberian. The area of Tomsk oblast is 316.9 km^2, which is larger than most European countries (Evseyeva 2001). Tomsk oblast borders with Krasnoyarsk Krai in the east, Tyumen and Omsk oblasts in the west, and Novosibirsk and Kemerovo oblasts in the south. This region includes 16 administrative districts (Fig. 1). The administrative center is the city of Tomsk. The region is inhomogeneous with the majority of the population living in the southern part of the Tomsk oblast near rivers, roads, and railroads.

The oblast is rich in natural resources, mainly in crude hydrocarbons (1.5 billion tons of oil and 757 billion tons of gas (Evseyeva 2001). The area is further characterized by a wide range of other types of mineral resources including sedimentary iron ores, complex zircon-ilmenite ores, occurrences of gold, platinum, zinc and bauxites, peat, and coal. In addition, Tomsk oblast is heavily forested with a total wood stock of 2760 million m^3 (Evseyeva 2001).

Its richness in natural resources is the main reason for the great number of industrial complexes in this region, which are associated with emissions of a large number of chemicals into the environment and related contamination and health problems. The biggest environmental problems of the region have been identified in the Tomsky district, where about 33 large industrial facilities of different sectors are situated. Among them, there are the country's largest petrochemical plant and the nuclear cycle plant as well as different energy processing and agro-industrial complexes. Additional zones, posing a potential threat for humans and the environment, mainly through soil contamination, include areas of oil and gas extraction and processing and buried radioactive waste as well as areas of intensive forest harvesting and fires (Rikhvanov et al. 2006).



Districts :
1- Alexandrovsky, **2** – Kargasoksky, **3** – Parabelsky, **4** – Kolpashevsky,
5 – Chainsky, **6** – Molchanovsky, **7** – Krivosheinsky, **8** – Shegarsky,
9 – Kozhevnikovsky, **10** – Tomsky, **11** – Asinovsky, **12** – Pervomaysky,
13 – Verkhneketsky, **14** – Teguldetsky, **15** – Zyriansky, **16** - Bakcharsky

Fig. 1 Geographical location of Tomsk oblast within the territory of the Russian Federation and its administrative division into districts (adapted from Evseyeva 2001)

Bromine soil inventory data

Soil sampling was carried out in the territory of Tomsk oblast between 2004 and 2015. Since sampling was carried out over a long period of time on a large area, it was necessary to maximally avoid the impact of possible external factors that could affect the concentration of the element in soils (for example, precipitations during sampling in one district and their absence in another). For this purpose, a methodological approach, consisting in synchronicity or maximum convergence of soil selection points in time, was used. Thus, all soil samples of the same year were taken across Tomsk oblast districts within the short period (3–5 days). In addition, it was also important to ensure the synchronicity of soil sampling in space. Therefore, the samples taken in each subsequent year were selected at identical points as the previous ones (GPS devices were used for this purpose). Sampling results are discussed in detail by Perminova et al. (2017) and are the starting point for obtaining the bromine soil inventory used in the present study. The following brief description summarizes the main sampling steps. Soils, used for agricultural purposes, were taken in 75 settlements in 14 out of the total of 16 administrative districts of the region, noting the presence or absence of organic fertilizers. The Alexandrovsky and Kargasoksky districts were not included in the study due to accessibility problems. The total number of soil samples was 384. Soil sampling from the topsoil 0–10 cm (the upper fertile layer) was conducted in the last decade of March to early April, using the "envelope" method. Five subsamples of 0.2 kg were selected from each soil pit, giving a total sample of 1 kg from each place. All samples were packed in thick wrapping paper. Pre-treatment of soil samples included the following steps: drying at room temperature, removal of foreign inclusions (vegetation particles, stones, etc.), grinding, and progressive sieving (initial sieve hole diameter was 2.5 mm, followed by 1 mm). All procedures were carried out according to normative standards (GOST 17.4.4.02-84, 1984). A subsample of 100 mg was packed in an aluminum foil for further analysis.

For the quantitative determination of bromine in soil samples, highly sensitive Instrumental Neutron Activation Analysis (INAA) was used. INAA is based on the detection of radioactive nuclides generated during the irradiation of test samples by a neutron flux. Irradiation was carried out by thermal neutrons with an integrated dose of 2×10^{13} n/(cm^2 s) at the research reactor IRT-T (Tomsk typical research reactor) of the Research Institute of Nuclear Physics at National Research Tomsk Polytechnic University in Tomsk, Russia. The sample exposure time was 20 h. The measurements were performed on a gamma spectrometer with a germanium-lithium detector. A comparative evaluation of the results obtained by the INAA with national (Russian) and international standards (IAEA) was carried out. The results were found to be satisfactory within the error of established concentrations of ± 5%. The data obtained from the INAA were analyzed in Microsoft Excel and Statistica 8.0 software to evaluate statistical parameters. All data are further described in Perminova et al. (2017).

Characterizing human toxicity and freshwater ecotoxicity

To characterize human toxicity and ecotoxicity impacts based on bromine soil concentrations from Perminova et al. (2017), we first calculated the total mass of bromine in agricultural soils of the region as follows:

$$m_i = C_i \times V_{\text{soil}} \times \rho_{\text{soil}} \tag{1}$$

with m_i ($\text{kg}_{\text{Br emitted}}$) the total bromine mass in agricultural soils of the region, calculated from the measured bromine concentration in soil identified by INAA, C_i (measured in $\text{mg}_{\text{Br in soil}}/\text{kg}_{\text{soil}}$ and multiplied by 10^{-6} to arrive at $\text{kg}_{\text{Br in soil}}/\text{kg}_{\text{soil}}$), the bulk soil volume in a considered region, V_{soil} (m^3_{soil}), and the bulk soil density, ρ_{soil} ($\text{kg}_{\text{soil}}/\text{m}^3_{\text{soil}}$).

We then applied version 2.02 of the UNEP-SETAC scientific consensus model USEtox (www.usetox.org), which is widely accepted for toxicity characterization in life cycle impact assessment and other comparative assessment frameworks (Westh et al. 2015). The substance databases of USEtox already include more than 3000 characterized organic substances and 27 metal ions. However, the inorganic substance bromine (CAS 7726–95–6) is not included. Hence, in our study, we aimed at developing human toxicity and freshwater ecotoxicity characterization factors (CFs) for bromine. Toxicity characterization factors express potential toxicity-related impacts on humans or ecosystems per unit of a particular chemical, emitted to a specific environmental compartment. Since USEtox is currently not applicable for inorganic substances other than metal ions, we developed preliminary CFs for bromine following, as the first proxy, the existing characterization in USEtox for both metal ions and organic substances, thereby acknowledging that both approaches have to be adapted to fully address the complex transformation of bromine in soils and potentially other media. This, however, is beyond the scope of the current study, where we focus on presenting a proof-of-concept framework for combining measured concentrations of soil contaminants consistently with multi-compartmental modeling to characterize impact on human toxicity and freshwater ecotoxicity, and identify associated future research needs.

For characterizing bromine, we calculate the cumulative toxicity impact score *IS* for a mass of chemical *x* (in our study bromine, Br) emitted to (or in our case initially present in) compartment *i* (in our study soil):

$$IS_{x,i} = CF_{x,i} \times m_i \tag{2}$$

with $IS_{x,i}$ as toxicity impact score (for human toxicity, disability-adjusted life years (DALY); for freshwater ecotoxicity, potentially disappeared fraction (PDF) of species integrated over exposed water volume and time, PDF m^3 d), $CF_{x,i}$ as a characterization factor (for toxicity-related impacts on human health, DALY/kg$_{\mathrm{Br\ emitted}}$; for ecotoxicity-related impacts on ecosystem quality, PDF m^3 d/kg$_{\mathrm{Br\ emitted}}$), and m_i as the chemical mass emitted or by extension in our case initially present in the soil compartment (kg$_{\mathrm{Br\ emitted}}$).

Characterization factors are derived from four factors, namely a fate factor, $FF_{x,i}$ (d) representing the residence time of the substance in soil; an exposure factor, $XF_{x,i}$ (for human exposure, kg$_{\mathrm{Br\ intake}}$/d per kg$_{\mathrm{Br\ in\ soil}}$; for ecosystem exposure, kg$_{\mathrm{Br\ bioavailable}}$/kg$_{\mathrm{Br\ in\ soil}}$); an effect factor, EF_x (for human toxicity effects, disease cases/kg$_{\mathrm{Br\ intake}}$; for freshwater ecotoxicity effects, PDF m^3/kg$_{\mathrm{Br\ bioavailable}}$), and a severity factor, DF, translating impacts into damages (for human health damages, DALY/disease case; for ecosystem quality damages, PDF/PAF with PAF as potentially affected fraction of exposed species):

$$CF_{x,i} = DF \times EF_x \times XF_{x,i} \times FF_{x,i} \tag{3}$$

As demonstrated by Heijungs (1995), the steady state assumption of a level III multi-media model like USEtox is equivalent to calculating the cumulative impacts of an initial pulse emission into soil (or in our case an initial mass in the soil at time zero), integrated up to infinity.

Calculated toxicity impact scores are therefore time-integrated, representing long-term impacts of the existing mass in soil. We discuss two scenarios for future emissions, i.e., assuming that there is no additional emission taking place, or assuming that there is a continuous constant emission flow corresponding to the present mass in soil divided by the residence time of the substance in soil. Fate, exposure, human toxicity, and ecotoxicity effect factors were derived following the USEtox approach. All input data used for calculating CFs for bromine are presented in Table 1.

Landscape data

Pre-defined landscape data in USEtox 2.0 are given for eight continental and 17 sub-continental regions and are mainly meant

Table 1 Data sources used for characterizing Br_2 as metal ion and organic substance in USEtox 2.02

Parameter, unit	Required to characterize Br_2 as organic (O) or inorganic (I) substance	Value	Reference
Molar mass, g/mol$^{(1)}$	I,O	159.81	Mendeleev's Periodic Table
Partitioning coefficient between octanol and water, l/l	O	10.72	US Environmental Protection Agency OPPTS (2010)
Solubility (at 25 °C), mg/l	O	17110	Gandolli (1999)
Vapor pressure (at 25 °C), Pa	O	28700	Lide (1993)
Partitioning coefficient between suspended solids and water, l/kg$^{(2)}$	I	55	IAEA International Atomic Energy Agency (2010)
Partitioning coefficient between sediment particles and water, l/kg$^{(2)}$	I	55	
Partitioning coefficient between soil particles and water, l/kg$^{(2)}$	I	55	
Rate constant degradation in air, 1/s	I,O	0.017	Fan and Jacob (1992)
Average of the log-values of the species-specific averaged eco-toxicity $EC_{50}$$^{(3)}$	I,O	– 0.27	According to the USEtox guidelines (Fantke et al. 2017)
Human-equivalent lifetime dose per person that causes a non-cancer disease probability of 50% after inhalation$^{(4)}$	I,O	0.058	
Human-equivalent lifetime dose per person that causes a non-cancer disease probability of 50% after ingestion$^{(5)}$	I,O	3.93	
Bioaccumulation factor in plant roots, kg$_{veg}$/kg$_{soil}$$^{(6)}$	I,O	0.3	US Environmental Protection Agency (2005)
Bioaccumulation factor in plant leaves, kg$_{veg}$/kg$_{soil}$	I,O	1.50	
Biotransfer factor in meat, d/kg$_{meat}$	I,O	0.025	
Biotransfer factor in milk, d/kg$_{milk}$	I,O	0.02	
Bioaccumulation factor in fish, l/kg$_{fish}$	I,O	160	Kennedy Jr and Strenge (1992)

$^{(1)}$ A molecule of bromine is diatomic; the molar mass taken into account was thus for Br_2

$^{(2)}$ According to IAEA 2009 (Appendix A-2), organic carbon does not play a major role in partitioning for metals and the same partitioning is assumed, regardless of the soil, suspended sediment or bottom sediment phase

$^{(3)}$ Original data source used is US Environmental Protection Agency 2005, where the acute EC_{50} for *Daphnia magna* is 1070 µg/l (see Table S1 in Supplementary Materials)

$^{(4)}$ Original data taken from http://gov.uk/government/uploads/system/uploads/attachment_data/file/316642/Bromine_guidance.pdf, where the LOAEL is 20 mg/kg bw/day, based on a subacute toxicity study in rats (see Table S2 in Supplementary Materials)

$^{(5)}$ Original data taken from https://echa.europa.eu/registration-dossier/-/registered-dossier/15150/7/6/3, where the NOAEC is 0.16 mg/m^3 , based on a subchronic toxicity study in rats

$^{(6)}$ Converted from dry weight to wet weight by dividing by a factor of 5 to be used as sensitivity analysis of default landscape parameters. The territory of the Russian Federation is among the available regions. However, since our study area covers only one region within Russia, we introduced a new set of landscape data reflecting the characteristics of the Tomsk oblast with an overview of all new landscape parameters given in Table 2.

Results

Distribution and sources of bromine in soils of Tomsk oblast

Measured concentrations of bromine determined in soils of the 14 districts of Tomsk oblast are summarized in Table 3 (adapted from Perminova et al. 2017), along with calculated total bromine mass in the soil of each considered district. Average concentrations of bromine across Tomsk oblast districts range from 9.3 mg/kg in Tomsky (measured mostly in natural soils, whereas soils in all other districts are agricultural soils) to 39.4 mg/kg in Bakcharsky with a minimum of 0.5 mg/kg in Kozhevnikovsky and Tomsky soils and a maximum of 64.9 mg/kg in Bakcharsky. Average concentrations of bromine in the studied soils remain within the mean worldwide contents (Kabata-Pendias 2010). However, the maximum concentrations of the element in two districts of the region (Tomsky and Bakcharsky) exceed the average world data. Bromine soil concentrations varied most in the Tomsky district (0.5–59.5 mg/kg) and least in the Shegarsky district (13–15.6 mg/kg). The histogram of the distribution of bromine content indicates close to normal distribution for the soils of the Tomsk oblast. When analyzing the distribution of bromine concentrations in the soils by district, we can observe that it is not conformed to the theoretical law on the normal distribution, with the exception of Kozhevnikovsky, Tomsky, and Bakcharsky districts (see Fig. S1 in Supplementary Materials). Across districts, bromine soil concentrations were on average 14.6 mg/kg and varied by a factor of 130 from minimum to maximum. As far as in Russia there are no any regulations for bromine in soils, we cannot conclude whether bromine concentrations found in soils meet or exceed a standard level.

In the soils of different districts of Tomsk oblast, various correlations of bromine with other chemical elements were found, which might be related to numerous factors. First, each district is characterized by non-identical natural and anthropogenic conditions. Secondly, soils vary considerably in their composition, characteristics, water regime, humus content, etc. All these aspects can influence both bromine occurrence forms and its migration and reactivity capacities in soils. For example, high variability in bromine soil concentrations of Tomsky district indicates a possible contribution from anthropogenic sources that is supported by the fact that bromine anomalies here are identified near pharmaceutical and petrochemical production plants,

Table 2 Landscape parameters used for characterization of Tomsk region in USEtox 2.02

Parameter	Value	Reference
Continental scale		
Area land, km^2	314000	Territorial body of the Federal State Statistics Service of the Tomsk region (2019)
Area fraction$_{\text{natural soil}}$ [−]	0.937	
Area fraction$_{\text{agricultural soil}}$ [−]	0.044	
Rain rate, mm/year	568	Evseyeva (2001)
Fraction run off [−]	0.464	Adapted from USEtox 2.02 for Central Asia
Fraction infiltration	0.269	Adapted from USEtox 2.02
Human population, capita	1.08 million	Territorial body of the Federal State Statistics Service of the Tomsk region (2019)
Urban scale		
Area land, km^2	33.6	Calculated in USEtox 2.02
Human population, capita	0.183 million	Territorial body of the Federal State Statistics Service of the Tomsk region (2019)
Production-based intake rates		
Above-ground produce, kg/(d capita)	0.362	Federal State Statistics Service (2019)
Below-ground produce, kg/(d capita)	0.677	
Meat, kg/(d capita)	0.167	
Dairy products, kg/(d capita)	0.71	
Fish freshwater, kg/(d capita)	0.0031	Federal Agency of Fishery (2019)
Fish coastal marine water, kg/(d capita)	0.046	

Table 3 Statistical parameters of measured bromine concentrations in the soils of the districts of the Tomsk region (mg/kg) (*n* = 384) and area-weighted averages across measurements⁽¹⁾ (adapted from Perminova et al. 2017—Table 2), complemented by district areas and calculated bromine mass in soil per district

No.	District	Area [km^2]	*N*	C_{Br}	λ	Min	Max	m_{soil} [million kg]
1	Alexandrovsky	29979	–	n/a				–
2	Kargasoksky	86857	–	n/a				–
3	Parabelsky	35846	6	14.8	1.7	9.0	22.1	30.71
4	Kolpashevsky	17112	6	11.9	2.1	7.5	21.3	24.69
5	Chainsky	7242	16	15.3	2.0	5.0	31.8	31.75
6	Molchanovsky	6351	5	14.5	1.1	11.1	18.0	30.09
7	Krivosheinsky	4400	2	16.8	–	13.0	20.1	34.86
8	Shegarsky	5030	2	14.3	–	13.0	15.6	29.67
9	Kozhevnikovsky	3908	33	18.2	1.5	0.5	35.8	37.56
10	Tomsky⁽²⁾	10039	177	9.3	0.4	0.5	59.5	410.92
11	Asinovsky	5943	15	19.7	1.8	5.0	31.8	40.88
12	Pervomaysky	15554	5	15.6	3.2	5.0	23.9	32.37
13	Verkhneketsky	43349	14	13.6	2.2	4.4	30.1	28.22
14	Teguldetsky	12271	20	13.2	1.4	5.0	28.0	27.39
15	Zyriansky	3966	44	10.8	1.0	3.9	34.4	22.41
16	Bakcharsky	24700	39	39.4	1.9	12.1	64.9	81.76

(1) *n/a*, no data available; *N*, number of samples; C_{Br}, average of measured concentrations; λ, standard error; Min and Max, minimum and maximum measured concentrations, respectively; m_{soil}, calculated bromine mass in soil.

(2) In this district, mostly natural soils near different industrial enterprises were taken

instrument-engineering and electric-bulb factories, and a Siberian chemical plant (nuclear industry). Soil samples of the Bakcharsky district on average showed the highest bromine contents, and are also characterized by significant correlations of bromine with a large number of other elements that might potentially be explained by the presence of iron ore deposits located in this district, where the bromine in the form of rare bromides may occur in the oxidation zones of some ore deposits.

Toxicity and ecotoxicity impacts of bromine

In Table 4, we summarize residence times, human intake fractions, and characterization factors for bromine, assumed to be released as continuous emission into agricultural and natural soils, by applying the characterization methods for metal ions and organic substances.

Residence times in soil, human intake fractions representing population intake of bromine per unit emission into soil, and related characterization factors for human toxicity and freshwater ecotoxicity are substantially higher when characterizing bromine as a metal ion compared with characterizing bromine as an organic substance for both agricultural and natural soils, with residence times in the range of years versus days, and intake fractions in the range of gram intake per kilogram emitted for bromine as metal ion versus milligram intake per kilogram emitted for bromine as organic substance, respectively. Regardless of whether bromine is characterized as a metal ion or as an organic substance, human intake fractions aggregated over inhalation and ingestion, as well as characterization factors for human toxicity, are substantially higher for emissions to agricultural soils by a factor 24 to 38 compared with emissions to natural soils. This is due to the dominant role of agricultural produce compared with other exposure pathways on the intake of bromine emitted to agricultural soils.

In addition, USEtox allows identifying the main exposure pathways and routes. It shows that for the characterization of bromine in soil as either substance form, the ingestion route is dominant, four to 22 orders of magnitude higher than inhalation, and that the three dominant pathways are via dairy product (associated with the 0.8 kg soil taken in daily by a cow (IAEA International Atomic Energy Agency 1994)), above ground produce and below ground produce (see Table S3 in Supplementary Materials).

Table 5 presents the total mass of bromine in the region and the resulting impact scores for human toxicity and freshwater ecotoxicity calculated with USEtox 2.02 for the entire Tomsk oblast region. Part a) of this table looks at the cumulative impacts of the initial mass measured in soil, assuming that there is no additional emission taking place, whereas part b) provides the steady state impacts assuming a continuous constant emission flow into soil.

Cumulative impact scores are on average a factor 200 higher for human health impacts and a factor 20 higher for ecosystem quality impacts when characterizing bromine the same way as metal ions are characterized compared with characterizing it the same way as organic substances are characterized (Table 5a). This is directly related to higher characterization factors for bromine if characterized as a metal ion, mostly based on much longer residence times in soil. These

Table 4 Residence time τ_{soil}, human intake fraction iF, and characterization factors CFs for Br_2 emissions in agricultural and natural soils as calculated with USEtox 2.02$^{(1)}$

Parameter	Br_2 treated as metal ion	Br_2 treated as organic substance
Emission to agricultural soil		
τ_{soil}	17.12 years	27.5 days
iF	7.06 $g_{Br\ intake}/kg_{Br\ emitted}$	30.59 $mg_{Br\ intake}/kg_{Br\ emitted}$
CF_{hum}	2.43×10^{-3} DALY/$kg_{Br\ emitted}$	1.05×10^{-5} DALY/$kg_{Br\ emitted}$
CF_{eco}	30181 PDF m^3 d/$kg_{Br\ emitted}$	2707 PDF m^3 d/$kg_{Br\ emitted}$
Emission to natural soil		
τ_{soil}	17.12 years	27.5 days
iF	0.29 $g_{Br\ intake}/kg_{Br\ emitted}$	0.79 $mg_{Br\ intake}/kg_{Br\ emitted}$
CF_{hum}	9.98×10^{-5} DALY/$kg_{Br\ emitted}$	2.75×10^{-7} DALY/$kg_{Br\ emitted}$
CF_{eco}	30181 PDF m^3 d/$kg_{Br\ emitted}$	2707 PDF m^3 d/$kg_{Br\ emitted}$

$^{(1)}$ τ_{soil}, residence time of Br_2 in soils extracted from the matrix of USEtox fate factors (in unit of time); iF, human intake fractions aggregated over inhalation and ingestion (in mass of Br_2 taken in by human population per kg of Br_2 emitted to soil); CF_{hum}, characterization factor for humans (in disability-adjusted life years (DALY) per kg of Br_2 emitted to soil); CF_{eco}, characterization factor for freshwater ecosystems (potentially disappeared fraction (PDF) of freshwater ecosystem species integrated over m^3 water volume and days of exposure duration per kg of Br_2 emitted into soil)

results demonstrate the importance of correctly characterizing fate transport and chemical transformation processes for substances, as we discuss in more detail below. It should be noted that it is only when considering bromine as metal ion that the residence time in soil of 17.12 years (Table 5b) is high enough to explain the observed soil concentrations. If bromine were mostly available in soils as organic substance form, the observed soil levels would imply an emission of more than 1 million of Br kg/d, which is not realistic.

Considering the case of the metal ion, the initial masses in soil are estimated by this model to generate impacts in the order of magnitude of 73500 DALY (Table 5a) for the entire regional population of 1.26 million, thus—as the first screening—an average of 0.06 DALY per person or in the order of 20 days of life lost per person on average, with 90% of the impact occurring within the next 40 years.

If continuous emissions would occur, maintaining the same measured levels in agricultural soil on the long term, the human health damages would amount to 11.8 DALY/d in the region, corresponding to an order of magnitude of 100 days of life lost over lifetime, where in all cases a life expectancy of 84 years is assumed in line with the Global Burden of Disease study series. As a screening indication, the steady state level of 11.8 DALY/d (Table 5b) corresponds to 4.4 new non-cancer disease cases per day for the 1.26 million inhabitants in the region; that is an incidence level of 126 non-cancer disease cases per 100,000 inhabitants per year associated with levels of bromine in soil. These numbers are associated with high uncertainties, especially due to the uncertainty of the toxicity effect factor, similarly to the factor 400 uncertainty reported by Fantke et al. (2012) for the total pesticide impacts in Europe (estimated at 2.4 h lost over lifetime per person). As a comparison element, ambient particulate matter impacts are estimated at an average (and substantially more accurate) value of 600 days of life lost per person over lifetime in Russia (ghdx.healthdata.org).

The spatial distribution of characterization results expressed as toxicity-related impact scores for human health and ecotoxicity-related impact scores for ecosystem quality closely follows the spatial distribution of measured soil concentrations, regardless of whether bromine is characterized as a metal ion or as an organic substance. The exception is Tomsky district, where emissions are made to natural soil, whereas in all other districts, we are

Table 5 Initial bromine mass in soils and toxicity impact scores of bromine in Tomsk oblast as calculated with USEtox 2.02 within cumulative impacts of existing mass (a) and impacts at steady state (b) for both bromine characterized the same way as metal ions and as organic substances, respectively

a) Cumulative impacts	$m_{Br\ in\ soil}$ [$kg_{Br\ emitted}$]	IS_{hum} [DALY]	IS_{eco} [PDF m^3 d]
Cumulative impacts of existing mass characterized as metal ion	3.03×10^7	73530	9.1×10^{11}
Cumulative impacts of existing mass characterized as organic substance	3.03×10^7	320	8.2×10^{10}
b) Steady state impacts	$\dot{m}_{Br\ in\ soil}$ [$kg_{Br\ emitted}$/d]	$\dot{IS}_{hum}$ [DALY/d]	$\dot{IS}_{eco}$ [PDF m^3]
Annual impact of steady state flow characterized as metal ion	$3.03 \times 10^7 / (17.12 \times 365) = 4850$	11.8	1.5×10^8
Annual impact of steady state flow characterized as organic substance	$3.03 \times 10^7 / (27.5) = 1.1 \times 10^6$	11.6	3.0×10^9

considering agricultural soils. This results in a very low impact score for human health in the Tomsky district, as impacts related to agricultural produce only play a minor role after emission to natural soil, even though the back-calculated emission mass is one order of magnitude higher compared with all other districts related to the much higher considered volume for natural soils in this region. On the other hand, Tomsky district shows the highest score for freshwater ecosystem impacts compared with all other districts, which is also related to the fact that emissions are assumed to be to natural soil in this region. Based on these results, impact scores for all considered districts can be ranked separately for human toxicity-related impacts and for freshwater ecotoxicity-related impacts, as shown in Fig. 2.

When ranking the different districts according to their impact scores for human toxicity and freshwater ecotoxicity impacts, our starting point is again the measured concentrations in soil. While bromine concentrations in natural soils of Tomsky district were lowest among all sampled regions, the volume of natural soil in this district is assumed to be much larger than the volume of agricultural soil, which leads to a higher back-calculated mass in natural soil and consequently results in higher potential impacts on ecosystems than in all other districts. This picture is reversed for human impacts, which are dominated by emissions into agricultural soil across all the districts (Fig. 2).

Ratios of human toxicity-related impact scores for each district and the highest impact score across districts indicate that the Bakcharsky district shows the highest potential for impacts on human health related to the highest bromine concentrations in agricultural soils, while the lowest potential impacts on human health are seen for the Tomsky district for emissions to natural soil. For all districts except Tomsky, emissions are into agricultural soil and ranking across districts therefore consistently follows the difference in measured soil concentrations (Fig. 2, top).

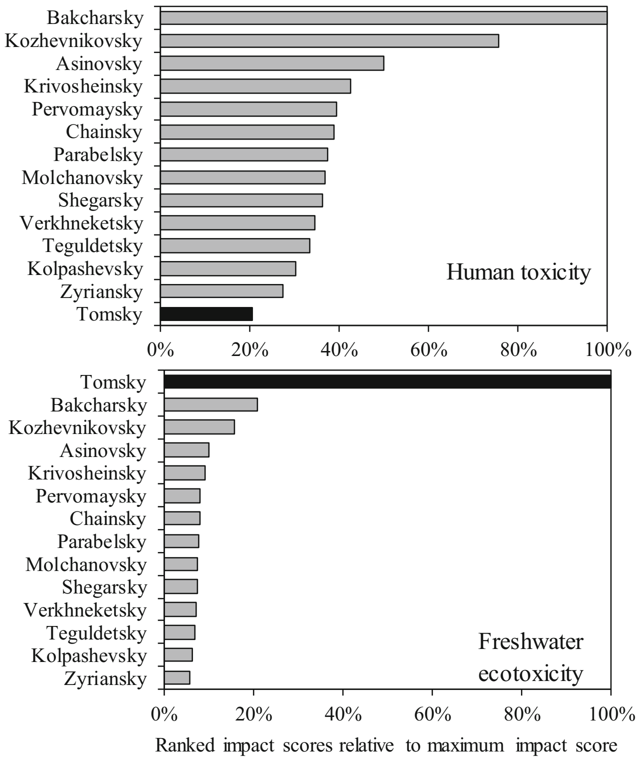


Fig. 2 Ranking of Tomsk oblast districts according to the ratio of their impact scores for human toxicity and freshwater ecotoxicity and the maximum impact scores across all districts, respectively. Black bars indicate natural soil; gray bars indicate agricultural soil

In contrast to the ranking of human toxicity impacts, ratios of freshwater ecotoxicity-related impact scores for each district and the highest impact score across districts show that the Tomsky district has the highest impacts on ecosystem quality following emissions to natural soil, while all other districts show consistently lower impacts following emissions to agricultural soil in line with the distribution of measured soil concentrations (Fig. 2, bottom).

These results stress the importance of properly defining the emission compartment, and related exposure pathways for humans and ecosystems.

Discussion

Applicability and limitations of analytical techniques

The INAA technique, applied in the study of Perminova et al. (2017) describing measured soil concentration, results as input to calculate bromine mass in soils of different regions. It determines total amounts of chemical elements regardless of their chemical and physical forms (liquid, solid, or gaseous) or oxidation state. Therefore, elements present in as ions, for example, are all determined as the generic form of the element. In the present study, relying on measured bulk bromine concentrations in soil as starting point, however, is a considerable limitation for identifying and potentially mitigating emission source contributions of the various emission forms to overall bromine-related soil pollution. This is because chemical form and kinetic pathways of emissions of bromine-related compounds are currently not considered when measuring bulk bromine concentrations. These pathways are complex and can have a significant influence on final pollution levels and related impacts of bromine, which is itself not emitted in its elemental form.

In addition, for toxicity characterization, we need to consider which fraction of bromine in soil is bioavailable, while the widely applied INAA technique only allows for determining total amounts of bromine in soils. Bioavailability in our study is hence accounted for as part of the environmental fate calculations implemented in the used toxicity characterization model.

To address the limitations of the INAA technique, another analytical method could be tested allowing for quantitative determination of different forms of bromine. For example, for the determination of bromide in soils, several methods could be used (e.g., potentiometric measurements and

Folgards method). However, in contrast to INAA, these methods are time-consuming and usually involve destructive solution of the sample that could influence the accuracy of the results obtained. Besides, the use of classical chemical methods of Br^{-} determination could be highly difficult to realize, since the separation of iodide and bromide ions in environmental objects is problematic due to the proximity of their redox potentials (Konarbaeva 2008).

Bromine chemistry in soil and implications for impact characterization

As no district-specific soil characteristics have been considered in our study, differences in soil concentrations are the only relevant driver for differences in the ranking across districts in terms of potential human health and ecotoxicity-related impact scores. However, for fully characterizing the environmental fate, exposure, and potential negative effects of bromine emissions to soil, it is thus not sufficient to know the available concentration of the overall bromine in soil. Instead, the different forms in which bromine and bromine compounds have originally been emitted have to be determined, which once again raises the question about analytical techniques to be used for the determination of bromine forms. Depending on the application of the particular substance, organic bromine compounds, such as bromoethane, bromopropene or bromoacetic acid, or inorganic bromine compounds, such as hydrogen bromide, hydrobromic acid, or alkali bromides and bromates, can all be emitted to soil, leading to different in-soil bromine profiles (Konarbaeva 2008). The different bromine compounds have different physicochemical properties compared with elemental bromine, which would also have to be considered in the impact characterization. These properties affect, among other issues, the reactivity, mobility, solubility, and other possible interactions in soil, which also depend on soil characteristics. Additionally, the bromine substances emitted undergo different chemical reactions leading to a variety of secondary products, which again have specific physicochemical properties and different bioavailabilities that would also have to be taken into account in the characterization modeling. For example, inorganic bromine in soil can react with organobromine compounds through enzyme reactions, abiotic metal catalysis, and photochemical reactions (Leri and Myneni 2012).

To better characterize the environmental exposure of bromine compounds in soil, the bioavailable fraction needs to be determined. Depending on soil conditions (e.g., pH, temperature) and interactions with soil components, such as organic matter, or other prevalent substances, the emitted bromine mass does not equal to the bioavailable bromine mass. A comparison of several studies has shown that the wide variation of bromine contents in soils can be traced back to two main factors of influence. First, bromine concentration in soil mainly depends on the soil moisture content, and second, the bromine content of soil is positively correlated with the content of soil organic matter (Flury and Papritz 1993; Neal et al. 2007; Moreno et al. 2017). Since soil properties can influence related bioaccumulation and toxicity of bromine, it is important to determine soil parameters along with bromine concentrations in soils. In our study, these parameters were not assessed at the sampling sites, constituting a limitation of the work. Further research efforts are thus required for consistently linking the effective bromine forms found in soil with their specific physico-chemical properties and reaction pathways with their respective bioaccumulation and toxicity potentials.

Besides, some bromine gases formed (like hydrogen bromide gas) are extremely soluble in water and quickly react with basic substances in soils (Kesner 1999). The resulting bromine ions do not lead to the toxicity in soils. Therefore, results obtained present an overestimation of toxicity impacts when bromine reaction chemistry in soils is not considered properly and when instead one has to rely on characterizing measured bromine soil content the same way as metal ions are characterized. A possible way to address this limitation is to report specific soil characteristics in future soil sampling results that can then be used to calibrate characterization model results.

Applicability and limitations of toxicity and ecotoxicity characterization

The most commonly used indicator for assessing potentially harmful effects of soil contamination levels in environmental studies is a standard defined as the maximum permissible concentration—MPC (Yazikov and Shatilov 2003; Chiroma et al. 2014). MPC values are usually established based on physicochemical substance properties, based on the results of biological or toxicological experiments, and are set by law or recommended by the competent bodies at local, national, or international level. However, such standards do currently not take into account transfer processes involving other environmental media or biota for relevant chemical reactions, all of which can influence possible negative effects on humans and ecosystems. Moreover, specific MPCs for bromine in soils are not currently set in Russia. Whenever MPCs were not available or cannot be used, background or Clarke values as well as literature data could, in some cases, be used as alternative instruments for assessing the contamination level. However, this is not always applicable (Bezuglova and Okolelova 2012), and usually faces the same limitations as MPCs regarding the combined consideration of fate, exposure, and toxicity aspects and pathways. In response, we demonstrated in the present study that linking measured soil concentrations to screening-level toxicity characterization results allows us to combine all the elements of the relevant impact pathways. Toxicity characterization results, however, should always be seen as being complementary to MPCs. This is important to ensure compliance with regulatory frameworks and at the same time to identify relevant tradeoffs between contributing pathways and aspects.

Furthermore, approaches like the one we presented here enable the comparison and ranking of results across relevant spatial regions (Tarasova et al. 2018). However, spatially different environmental conditions and their influence on impact results cannot be considered using environmental standards/limit values which are the same for the entire territory of a country, which is often criticized (Limanova 2005). This aspect is especially relevant for bromine, which shows considerable variability in migration characteristics and interactions with other substances, all of which is highly dependent on the specific environmental conditions. Besides, scaling chemical pollution and related impacts is a key issue for large countries, like for example Russia, Canada, or China. The large size of a territory often involves large differences in climatic, hydrogeological, morphological, and other conditions, which can greatly affect the impact potential of chemical pollutants on the environment or on human health within the same territory. By integrating region-specific landscape data, we could make our study more reliable in terms of representing environmental conditions.

Additional limitations occur in the characterization approach. In order to calculate time-integrated impact scores for human toxicity and ecotoxicity in different districts of Tomsk oblast, the average bromine concentration within each district was used to back-calculate the emitted mass in the respective soils. This will not reflect the actual variability in soils within a district. Related to that, neither differences in soil characteristics within nor between districts were considered, nor could the contribution of different potential sources of measured bromine in soil be back-calculated. This would be relevant for identifying and mitigating the most relevant pollutant sources in the Tomsk oblast.

Another limitation in our study is the number of trophic levels used for calculating the ecotoxicological effect factor for bromine, which is currently based only on data for one trophic level due to the limited availability of underlying data. In addition, terrestrial ecotoxicity is currently not included in the current version of the USEtox consensus model and, hence, this impact pathway needs to be included to evaluate possible impacts of bromine amounts in soil on terrestrial ecosystems including soil organisms.

Finally, in addition to exposure determination, the human toxicity dose-response factor is a main source of uncertainty that can vary considerably between individual chemicals and chemical species (Fantke et al. 2012; Fantke and Jolliet 2016).

Future research required to improve bromine characterization

Estimating human toxicity and ecotoxicity impact scores for bromine under assumed steady state conditions and by characterizing this substance currently the same way as a metal ion or as an organic substance ignores the complex but important reaction pathways of the actual emitted bromine-related compounds with their specific bioaccumulation and toxicity potentials. To improve the toxicity and ecotoxicity characterization when measured soil concentrations are given, a dynamic fate modeling approach should be followed, where emissions are not assumed continuous, but could be modeled as pulse(s) or periodic emissions (Ngole-Jeme and Fantke 2017). This would allow to emphasize further potential differences in pollutant dynamics.

In addition to changing the system's time horizon, the modeling approach regarding fate and effect has to be adapted to bromine and its compounds to improve the toxicity and ecotoxicity characterization. In contrast to organic chemicals, and for most inorganic substances, an approach mainly based on Kow is not suitable for characterizing the various environmental fate and transformation processes of bromine and related substances in soil. For example, the concentration of emitted bromide salts might not equal the bioavailable fractions of these substances, as it is strongly dependent on soil conditions such as pH and temperature as well as the organic matter content. This highlights the importance of soil parameters to be taken into account. In addition, the chosen approach of converting acute effect data to chronic ecotoxicity effect data with a fixed acute-to-chronic correction should be reviewed for bromine and bromine compounds. Dong et al. (2014), for instance, show that this factor for particular metals varies substantially, especially for different tested trophic levels or species. Overall, our characterization approach can serve as the first screening of bromine impacts on humans and the environment, but will have to be linked to specific bromine emissions in order to refine the assessment.

Conclusions

Our study demonstrates how measured concentrations of chemicals in soil can operationally be combined with screening-level toxicity and ecotoxicity characterization models tailored toward a specific region of interest, based on adapting region-specific landscape data. This approach suggests considering fate and exposure processes as well as related potential human toxicity and ecotoxicity impacts in environmental studies, thereby adding an important sustainability-related dimension that is required to assess and evaluate possible trade-offs between impacts and regions and ultimately linking such impacts to physical limits for chemical pollution to achieve environmental sustainability (Fantke and Illner 2019). Region-specific landscape data together with analytical techniques for identifying bromine concentrations in soils allows different considered districts to be ranked according to the potential impacts on ecosystems and human health caused by their different soil concentration levels. The approach followed, however, currently lacks any consideration of the complex soil chemistry of emitted bromine compounds, which is required for more accurate toxicity impact factors. Hence, existing toxicity characterization models need to be adapted in terms of considering the chemical reaction and transfer pathways of bromine and other inorganic compounds from emission to the affected receptors, and in terms of considering chemical species-specific toxicity information. Overall, our approach already helps complementing existing evaluations of soil pollutant levels with information on potential toxicity-related impacts on humans and ecosystems, and outlines how characterization models should better account for reaction kinetics of inorganic substances (Kirchhübel and Fantke, 2019). This is an important input to inform pollutant mitigation strategies in regions like the Tomsk oblast. Lastly, the combined consideration of fate, exposure, and (eco-)toxicity impacts could be considered in some standardization processes, by contributing to cover certain missing existing limits.

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