Types of synthetic cannabinoids seized from illicit trafficking in the territory of the Siberian Federal District (Russia) between 2009-2018

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A B S T R A C T

Background: in the last decade, new psychoactive substances including synthetic cannabinoids (SC) have appeared and are rapidly spreading in the Siberian Federal District of Russia. The determination of the individual composition of the synthetic cannabinoids is very important, first of all, for assessing the risk of harming the health of potential consumers as well as for determining sources of their appearance.

Objective: to describe the types of synthetic cannabinoids, the dynamics of their occurrence and distribution in the illegal market of drugs in the territory of the Siberian Federal District (Russia) for the period from January 2009 till December 2018. Compare the results obtained with the SC distribution trends in other countries.

Method: a retrospective analysis of databases (narcotic reports, chromatograms, mass-spectrums) obtained from GC-MS studies of 2142 samples taken from illicit trafficking in the territory of the Siberian Federal District (Russia) from January 2009 to December 2018 was conducted.

Results and conclusion: during the analyzed period, 62 individual SCs of various types were identified in the studied samples. Of these, the AB-PINACA-CHM, MDMB(N)-2201, CBL-2201, TMCP-2201 were found most frequently (10-24% cases). In single cases JWH-018-Br, JWH-018-CI, JWH-019, MBA-2201 and QCBL(N)-2201 were identified. The share of the other identified individual SC did not exceed 10%. The results obtained are compared with the SC distribution trends in some countries of the Asia-Pacific region, the European Union and Turkey. Creating an objective global picture of the prevalence of SC requires a unified approach to the provision of relevant representative data.

Keywords: synthetic cannabinoids, illicit drugs seizure, Siberian Federal District, Russia

1. Introduction

Synthetic cannabinoids in the illegal market of drugs are one of the world problems [1]. The works [2-13] demonstrate the results of the studies according to the types and distribution of synthetic cannabinoids in some countries of the Europe, middle East and the Asia-Pacific Region. In Russia, the withdrawal of smoking blends containing SC from illicit trafficking has been recorded since 2009. In the Siberian Federal District of Russia, the territory of which is 5.1 mln sq. km. (30% of the territory of Russia), and the population is more than 19 mln people, the estimation of types of synthetic cannabinoids in the drug cases was performed by the Expert and Criminalistic Center of the Transport Administration of the Ministry of the Interior of the Russian Federation in the Siberian Federal District and the former Main Directorate of the Federal Drug Control Service of the Russian Federation in Krasnoyarsk Krai. A large amount of data was accumulated in the form of reports, databases, chromatograms and mass spectra. It was interesting to systematize the initial data and to perform the retrospective analysis of the accumulated material due to the extension of the list of dangerous synthetic cannabinoids, updating of the libraries of mass spectra to identify the types of synthetic cannabinoids and tendencies of their distribution at the regional level. The latter seems to be a rather important additional factor for the formation of the objective problem of synthetic cannabinoids at the global level and development of the adequate measures for its solution. This study was performed with the permission of the Management of the Expert and Criminalistic Center of the Transport Administration of the Ministry of the Interior of the Russian Federation in the Siberian Federal District.

2. Materials and methods

2.1. Materials

The samples containing synthetic cannabinoids were seized by the police from the user or the dealer between January 2009 and December 2018 (in all 2142 samples). The analyzed samples, as a rule, were solid, plastic or powdery substances of different colors as well as dried plant fragments of different dispersion.

2.2. Solvent and Sample preparation

Samples for the study were milled in porcelain mortars to a homogeneous state. Next, sub-samples of 2-5 mg in the case of powdered substances and 10-15 mg in the case of plant mixtures or plastic substances were extracted with 1 ml of methanol (purity not lower than analytical grade). The resulting solutions were incubated for 30 minutes at room temperature, then centrifuged to separate the residue and further investigated by the method of GC-MS.

2.3. Instruments and parameters of GC-MS method

Samples were studied according to recommendations [14, 15]. GC–MS analysis were performed with a chromatograph Kristall 5000.2 (Russia) with a quadrupole mass-spectrometer detector (MCD) ISQ (Thermo Scientific), a chromatograph Agilent 6890 with a quadrupole mass-spectrometer detector 5973 (Agilent Technologies). Analysis conditions: electron impact ionization (power of 70 eV); fused silica columns 30 m in length and 0.32 mm in diameter, with a methylpolysiloxane phase containing 5% of phenyl groups (type HP-5MS); evaporator temperature - 280°C; detector interface temperature – 280°C; initial column temperature – 100°C; final column temperature – 300°C; rate of column temperature elevation – 15°C/min; holding time at the final temperature - 10 min; carrier gas - helium; carrier gas flow rate – 1.0 ml/min; sample injection mode – split (Split 40:1).

2.4. Identification of mass spectra

Evaluation of the similarity of the mass spectra was carried out after the library search. The following libraries were used: open-source: SWGDRUG, Cayman Spectral Library and departmental libraries of psychoactive substances (EKBDRUGS). The mass-spectra with the values of similarity index above 850 units were taken into account. From the identification hypotheses proposed by the software, the variant with the highest value of the similarity index was chosen. At the following stage, a comparison was made of the presence of peaks of all characteristic ions and their intensities. Special attention was paid to the peak of the molecular ion and to the peaks of ions with intensities of more than 5% of the intensity of the maximum ion. Mass spectra were considered to match if the peaks of all characteristic ions from the library mass spectrum were present in the investigated mass spectrum, including the molecular ion in the absence of extraneous ion peaks, especially with intensities of more than 3%.

3. Results and discussion

JWH-018 was detected in three samples seized from illicit trafficking in September 2009. There are 62 types of different SC were identified in samples in subsequent 9 years (Table 1).

Table 1.

Number of SC containing samples seized from illicit trafficking between 2009-2018

SC name/year	2010	2011	2012	2013	2014	2015	2016	2017	2018	Total number
A-836,339	0	2	0	0	0	0	0	0	0	2
AB-FUBINACA*	0	0	0	4	3	21	26	27	2	83
AB-PINACA	0	0	0	32	14	15	12	0	0	63
AB-PINACA-CHM	0	0	0	9	23	344	125	2	3	506
AB-PINACA-F*	0	0	0	9	1	29	7	0	0	46
ACBM(N)-018	0	0	22	10	3	4	0	0	0	39
ACBM(N)-2201*	0	0	32	49	2	0	0	0	0	83
ACBM(N)-BZ-F*	0	0	0	0	0	7	0	0	0	7
ACBM-018	0	0	3	2	0	0	0	0	0	5
ACBM-022	0	0	5	0	0	0	0	0	0	5
ACBM-2201*	0	0	18	8	0	0	0	0	0	26
ADB-CHMINACA	0	0	0	0	3	74	19	0	0	96
ADB-FUBINACA*	0	0	0	0	0	4	28	20	0	52
ADB-PINACA	0	0	0	0	2	0	2	0	0	4
AM(N)-2201*	0	0	0	1	41	10	1	0	0	53
AM-2201*	0	2	49	6	0	0	0	0	0	57
AM-694*	0	6	0	0	0	0	0	0	0	6
AMB-FUBINACA*	0	0	0	0	0	0	37	60	0	97
BIM-018	0	0	0	0	0	6	6	0	0	12

BzCBM-018	0	0	0	0	0	2	0	0	0	2
CB-13	0	0	0	0	0	0	2	0	0	2
CBL(N)-2201*	0	0	0	0	0	9	8	0	0	17
CBL-2201*	0	0	0	29	60	67	69	0	3	228
CBL-BZ-F*	0	0	0	1	9	5	12	0	2	29
CBM-018	0	0	3	2	0	0	0	0	0	5
CP 47,497-C8	8	0	0	0	0	0	0	0	0	8
EAM-2201*	0	0	0	8	0	1	0	0	0	9
EDMB(N)-2201*	0	0	0	0	0	3	13	0	4	20
JWH-018	105	7	6	33	1	0	0	0	0	152
JWH-018-Br	0	0	0	1	0	0	0	0	0	1
JWH-018-Cl	0	0	0	1	0	0	0	0	0	1
JWH-019	0	0	1	0	0	0	0	0	0	1
JWH-073	39	2	0	0	0	0	0	0	0	41
JWH-122-F*	0	0	0	3	0	0	0	0	0	3
JWH-203	41	35	23	2	2	0	1	0	0	104
JWH-210	0	3	38	5	0	4	0	0	0	50
JWH-250	41	13	1	1	0	0	0	0	0	56
JWH-251	1	0	1	2	0	0	0	0	0	4
JWH-307	0	0	0	0	0	6	2	0	0	8
JWH-022	0	4	0	0	0	0	0	0	0	4
MAM-2201*	0	0	2	32	0	0	0	0	0	34
MBA-CHM	0	0	0	0	0	6	2	0	0	8
MBA-2201	0	0	0	0	0	1	0	0	0	1
MDMB(N)-2201*	0	0	0	0	0	67	96	101	204	468
MDMB(N)-BZ-F*	0	0	0	0	0	12	4	0	0	16
MDMB-2201*	0	0	0	0	0	0	0	0	2	2
MDMB-BZ-F*	0	0	0	0	1	20	0	0	0	21
MDMB(N)-073-F*	0	0	0	0	0	0	0	0	2	2
MDMB-CHM	0	0	0	0	10	11	9	0	0	30
MMB(N)-2201*	0	0	0	0	7	73	45	0	2	127
MMB-2201*	0	0	0	0	9	0	22	0	0	31
PPA(N)-2201*	0	0	0	0	0	5	3	0	0	8
PPA-2201*	0	0	0	0	1	7	9	0	0	17
QCBL(N)-2201*	0	0	0	0	1	0	0	0	0	1
QCBL-018	0	0	14	37	4	0	0	0	0	55
QCBL-2201*	0	0	1	26	19	17	2	0	0	65
QCBL-BZ-F*	0	0	0	1	12	0	5	0	0	18
QCBL-CHM	0	0	0	0	4	0	0	0	0	4
RCS-4	0	3	7	1	0	0	0	0	0	11
TMCP-018	0	1	12	11	4	46	12	0	0	86
TMCP-2201*	0	0	31	2	70	29	6	19	63	220
TMCP-CHM	**0**	0	0	0	0	0	0	0	19	19

* fluorinated synthetic cannabinoids.

MS-spectrums of the identified SCs are collected in the MS-library (*.msp format) and in the table 3, which are attached to this publication.

A total of 3231 cases of individual SCs detection were recorded in 2142 samples. The latter is explained by the fact that some samples contained several active agents (Fig. 1).

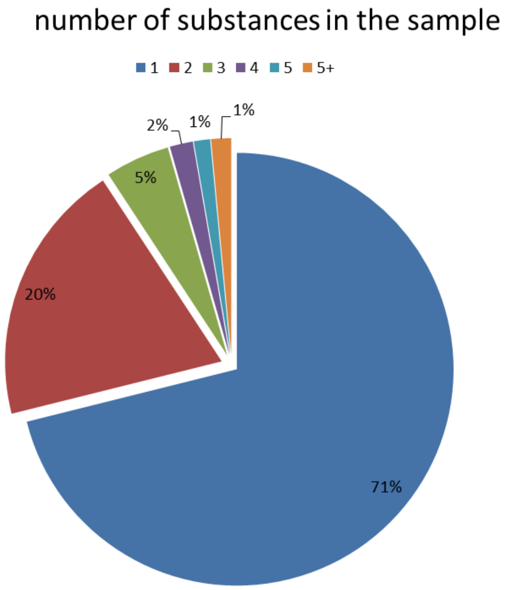

Fig. 1. Shares of samples containing a particular amount of synthetic cannabinoids.

Table 1 shows that the majority of samples seized during the entire period contained the following SC: AB-PINACA-CHM, MDMB(N)-2201, CBL-2201 and TMCP-2201 (10-24 % cases). In single cases JWH-018-Br, JWH-018-CI, JWH-019, MBA-2201 and QCBL(N)-2201 were identified. The share of the other identified individual SC did not exceed 10%.

To describe the type dynamics of SC, the scheme of the European Monitoring Centre for Drugs and Drug Addiction (EMCDDA) was used: Linked Group – Tail – Core – Linker (Fig. 2) [16].

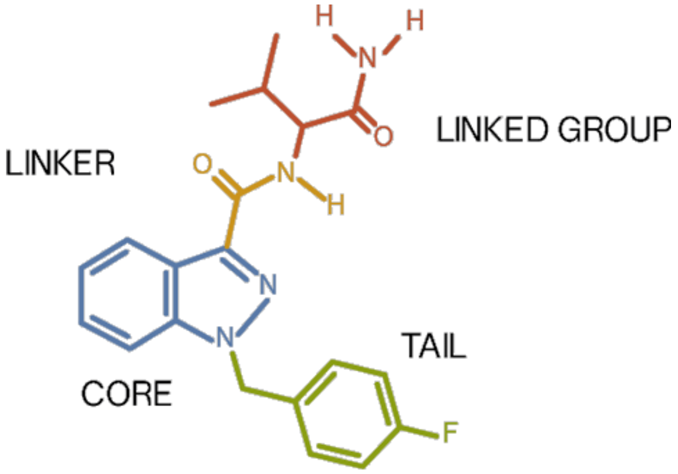

Fig. 2. Structural fragments of SC according to the scheme EMCDDA.

During 2010-2011, SC of the first generation from the class of naphthoylindoles, phenylacetylindoles and benzoylindoles were identified mostly in the studied samples: JWH-018, JWH-073, JWH-203, JWH-210, JWH-250, JWH-251, JWH-022. The share of naphthoylindoles was the biggest among the withdrawn samples. A good correlation of the prevalence of these types of SC in the territory of the SFD (Russia), Japan and South Korea is observed [6, 7].

2012-2013 are characterized by the significant amount of SC with new tail, attached and connecting groups and well as core components.

The new tail groups: 4-fluorobenzyl (AB-FUBINACA), cyclohexylmethyl (AB-PINACA-CHM), 5-fluorpentyl (AM-2201, MAM-2201).

The new attached groups: adamantyl (ACBM(N)-018, ACBM(N)-2201, ACBM-018), tetramethylcyclopropyl (TMCP-018, TMCP-2201).

The new connecting groups: carboxamide (ACBM-018) and carboxylate (QCBL-2201).

The new core components are indazole containing SC (ACBM(N)-2201, ACBM(N)-018, QCBL-018, QCBL-2201).

During this period, about 30 types of SC with similar structures were detected in European countries and about 50 SC in Japan [6, 16]. In South Korea the SC from the class of quinolinecarboxylates (QCBL-018, QCBL-2201) were widespread [7]. The comparative data from Turkey show that some SC (ACBM(N)-018), MAM-2201, TMCP-2201) were observed in 2013 and in the territory of the SFD (Russia) they were observed in 2012 [11].

Since 2014, almost complete disappearing of SC with the JWH structure from the illicit trafficking has been observed. The new structural element that appeared in 2014 is an attached 1-methoxycarbonylalkyl group in such SC as: MMB(N)-2201, MDMB-BZ-F, MDMB-CHM.

In 2015-2016, almost all compounds that appeared again in trafficking were referred to the substances of the attached 1-methoxycarbonylalkyl group such as AMB-FUBINACA, MDMB(N)-2201. At the same time, there was a decrease in the number of cases of withdrawal of substances from the classes of indole-3-carboxylates (QCBL-2201), indazole-3-carboxamides (ACBM(N)-2201), and cyclopropylindoles (TMCP-2201).

The period 2017-2018 was characterized by a decrease in species diversity and a lack of SC with new structural elements. Most often in the withdrawn samples was found MDMB(N)2201 – SC of carboxamide group, as well as SC with tetramethylcyclopropyl group (TMCP-2201).

In general, there was a significant decrease in the incidence of SCs with a JWH structure and an increase in the proportion of SCs of the carboxamide group over the study period (Fig. 3). SC-containing samples of the carboxylates group were the most common in 2013-2015, but have practically disappeared from illicit trafficking by now.

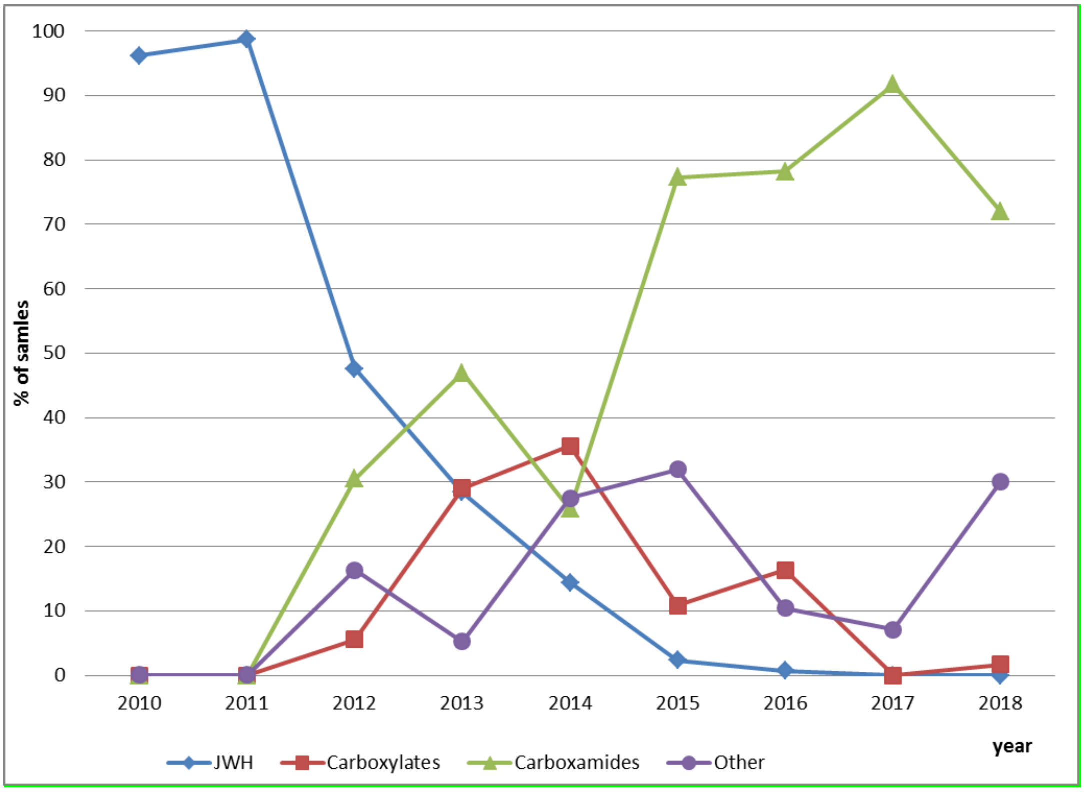

Fig. 3. Share of SC-containing samples of different structure seized from illegal circulation in the territory of the SFD (Russia) between 2010 – 2018.

The fluorine-containing SC took a rather significant share of the total number of SC samples withdrawn in the territory of the SFD (Russia) (Table 1) with a higher bioactivity in comparison with their unsubstituted analogues (Fig. 4). Some decrease in their share in 2015 and 2016 can be explained by the wide distribution of AB-PINACA-CHM. The mentioned tendency was also observed in South Korea: it was reported that 90% of SC seized in 2013 were fluorinated, compared with 60% in 2012, and just 15% in 2011, with none reported before 2011 [7].

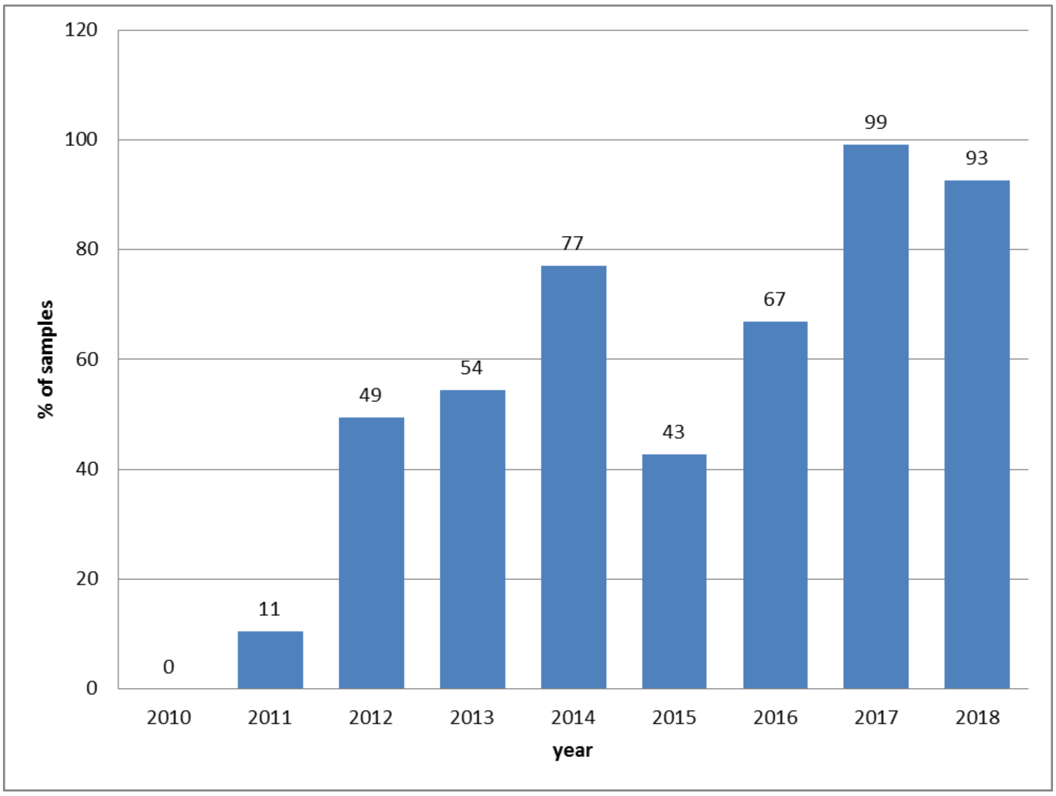

Fig. 4. Share of samples with fluorinated SC, seized from illegal circulation in the territory of the SFD (Russia) between 2010-2018.

However, a full comparative analysis of the species prevalence of the SC in various countries for 2010-2018 is largely difficult due to the lack of representativeness of the available data. Table 2 shows information on the most common SCs in the Siberian Federal District (Russia) and some other regions (countries) based on the results of this study and scientific publications [3-13, 16-19].

Table 2.

The cannabinoids with the highest overall quantities seized in different times in some territories.

Year	SC name	Territory
2010	CP 47,497-C8 JWH-073 JWH-203 JWH-250 JWH-018	SFD (Russia)
2011	JWH-203 JWH-250 JWH-018 AM-694 JWH-022	SFD (Russia)
2012	AM-2201 JWH-210 ACBM(N)-2201 TMCP-2201 JWH-203	SFD (Russia)
	MAM-2201 AM-1220 QCBL-018 ACBM(N)-018 TMCP-2201	Japan [6]
2013	ACBM(N)-2201 QCBL-018 JWH-018 AB-PINACA CBL-2201	SFD (Russia)
	QCBL-2201 TMCP-2201 TMCP-018 QCBL-CHM EAM-2201	Japan [6]
2014	TMCP-2201 CBL-2201 AM(N)-2201 AB-PINACA-CHM QCBL-2201	SFD (Russia)
	AM-2201 MDMB-CHM AB-FUBINACA MAM-2201 TMCP-2201	Europe[17]
2015	AB-PINACA-CHM ADB-CHMINACA MMB(N)-2201 CBL-2201 MDMB(N)-2201	SFD (Russia)
	ADB-FUBINACA ADB-CHMINACA AB-PINACA-CHM TMCP-018 ACBM(N)-2201	Europe [18]
	ADB-FUBINACA ADB-CHMINACA AB-FUBINACA AM-2201	Turkey [11]
2016	AB-PINACA-CHM MDMB(N)-2201 CBL-2201 MMB(N)-2201	SFD (Russia)

	AMB-FUBINACA	
	CBM(N)-2201 CUMYL-4CN-BINACA AMB-FUBINACA MDMB(N)-2201 AB-FUBINACA	Europe [19]
	MDMB(N)-2201 ADB-FUBINACA CUMYL-4CN-BINACA ACBM(N)-2201 ADB-CHMINACA	Turkey [12]
2017	MDMB(N)-2201 AMB-FUBINACA AB-FUBINACA ADB-FUBINACA TMCP-2201	SFD (Russia)
2018	MDMB(N)-2201 TMCP-2201 TMCP-CHM EDMB(N)-2201 AB-PINACA-CHM	SFD (Russia)

4. Conclusion

The analysis of the mentioned data demonstrates that the territory of the SFD (Russia) is not a "periphery" in the world illegal market of drugs. The occurrence and distribution of new types of SC has a global nature and is reproduced with a significant similarity in many countries, although with some regional specific character. Creating an objective global picture of the SC distribution and reducing the influence of random and local factors requires the development of a unified form of presenting information not only on the types of newly identified substances, but also on their quantities taken out of illegal traffic. Sharing such data can improve the understanding of the causes of differences in the prevalence of certain types of SC and will help directing the efforts of scientists, law enforcement agencies and health authorities to work with the most relevant substances.

Appendix A. Supplementary data (Table 3, MS-library)

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