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基于畜禽粪便的有机肥中雌激素污染特征

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摘要:为了解基于畜禽粪便的有机肥中残留雌激素的污染特征,防控有机肥生产中的污染风险。采集了市面上基于鸡粪、猪粪、牛粪制备的17种有机肥,测定了其有机质、氮、磷和钾含量;采用SPE-HPLC/FLD法检测了样品中雌三醇(E3)、17 β -雌二醇(17 β -E2)、双酚A(BPA)、炔雌醇(E2)四种雌激素的含量,并将结果与新鲜鸡粪、猪粪、牛粪中四种雌激素含量进行对比。结果表明,鸡粪、猪粪和牛粪有机肥中均存在有机质含量偏低的样品;鸡粪有机肥中E3、17 β -E2、BPA均值(干质量计)分别为270.22、2.71、87.93 $\mu\text{g}\cdot\text{kg}^{-1}$;猪粪有机肥中E3、17 β -E2、BPA、EE2均值为609.71、41.84、32.69、46.74 $\mu\text{g}\cdot\text{kg}^{-1}$;牛粪有机肥中E3均值为50.96 $\mu\text{g}\cdot\text{kg}^{-1}$ 。畜禽粪便有机肥存在雌激素污染风险,且E3风险最大。所检测的三种畜禽粪便制备的有机肥中,牛粪有机肥雌激素含量、检出率均最低。有机肥中E3、17 β -E2、BPA、EE2检出率分别为47.06%、11.76%、17.65%、5.88%,四种雌激素在新鲜粪便中检出率则为67.74%、70.97%、70.97%、58.06%,有机肥中雌激素检出率低于新鲜畜禽粪便。综上所述,基于畜禽粪便的有机肥中仍会有雌激素残留,应引起重视。

关键词:畜禽粪便;鸡粪;猪粪;牛粪;有机肥;雌激素;检出率

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Characteristics of estrogen contamination in organic fertilizers derived from livestock manures

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Abstract: Understanding estrogen contamination characteristics of organic fertilizers derived from livestock manures is important for organic fertilizer production and contamination control. In the present study, 17 organic fertilizers derived from chicken, swine, and cow manures were collected from a market. Organic matter, nitrogen, phosphorus, and potassium contents of organic fertilizers were determined. The concentration of estradiol (E3), 17 β -estradiol (17 β -E2), bisphenol A (BPA), and ethinyl estradiol (EE2) were detected by SPE-HPLC/FLD. At the same time, we compared the estrogen concentrations in organic fertilizers with fresh livestock manures. Results showed that organic fertilizers with low organic matter were detected in the organic fertilizer samples derived from chicken, swine, and cow manures. The average value (dry weight) of E3, 17 β -E2, and BPA in organic fertilizers derived from chicken manures were 270.22, 2.71 $\mu\text{g}\cdot\text{kg}^{-1}$, and 87.93 $\mu\text{g}\cdot\text{kg}^{-1}$, respectively. The average values of E3, 17 β -E2, BPA, and EE2 in organic fertilizers derived from swine manures were 609.71, 41.84, 32.69 $\mu\text{g}\cdot\text{kg}^{-1}$, and 46.74 $\mu\text{g}\cdot\text{kg}^{-1}$, respectively. The average value of E3 in organic fertilizers derived from cow manures was 50.96 $\mu\text{g}\cdot\text{kg}^{-1}$. Organic fertilizers had a large risk of estrogen contamination, and the risk of E3 contamination was higher than that of the other estrogens. Additionally, the concentration and detection rates of estrogen in cow organic fertilizers were lower and safer. The detection rates of

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E3, 17 β -E2, BPA, and EE2 in organic fertilizers were 47.06%, 11.76%, 17.65%, and 5.88%, respectively, while detection rates were 67.74%, 70.97%, 70.97%, and 58.06% in fresh livestock manures, respectively. The detection rates of estrogen in organic fertilizers were lower than that of fresh livestock manures. The conclusion is that there are estrogen residues in organic fertilizers derived from livestock manures, which needs further attention.

Keywords: livestock manures; chicken manure; swine manure; cow manure; organic fertilizers; estrogen; detection ratio

有机肥又称农家肥,具有成分复杂、肥效长、养分全面等特点。农业生产中施用有机肥,可增加土壤肥力、提高作物产量和改善品质,其施用效果得到普遍肯定^[1-3]。随着人们对食品安全意识的提高,生态农业和绿色食品愈来愈受到重视,使得有机肥料的应用也越加广泛^[4]。有机肥料原料来源丰富,如人畜粪便、堆沤肥、污泥、绿肥、杂肥及各种垃圾等^[5]。近年来集约化禽畜养殖业快速发展,禽畜粪便成为有机肥主要来源^[6]。

雌激素是由动物体内细胞所分泌出来的一种化学物质,能够协调生物体各种生理过程^[7]。但排入环境中的雌激素会通过模拟、干扰机体内生激素原有的正常合成、运输和释放,使其无法维持自身的平衡和调节,可引起人类和动物的雌性化^[8-9]。作为雌激素重要来源之一的养殖业畜禽粪便,会携带大量的雌激素^[10-11]。通过施肥进入农业土壤,对环境、动物及植物等造成不良的影响,并最终会随食物链影响人类健康^[12]。有机肥料中雌激素污染状况及其施用的生态安全研究已刻不容缓。

鉴于畜禽粪便有机肥对土壤及生态环境存在的潜在危害,国内外已针对其中的重金属和抗生素污染展开大量研究^[13-15],并对有机肥中各种污染物制定了一系列安全标准^[16-18]。但关于有机肥中雌激素污染鲜有报道,并且已有标准中没有具体指标涉及雌激素的残留问题。有关有机肥中雌激素的污染特征数据极度缺乏,市面上经生物发酵的有机肥中雌激素污染状况尚不明确。本文收集了17个畜禽粪便商品有机肥样品,检测了有机肥中雌激素的种类和含量,分析畜禽粪便制成的有机肥中雌激素的污染特征,为阐释有机肥中雌激素对环境的危害提供重要理论依据。

1 材料与方法

1.1 雌激素标准品及商品有机肥

雌三醇(E3, 98%)、17 β -雌二醇(17 β -E2, 98%)、双酚A(BPA, 99%)标准品均购自上海晶纯试剂有限公司,炔雌醇(EE2, 99%)标准品购自美国Sigma公司。甲醇(色谱纯)、乙酸乙酯(分析纯)和乙腈(色

谱)购自南京化学试剂股份有限公司。共收集商品有机肥样品17个,其中9个鸡粪有机肥样品、4个猪粪有机肥样品和4个牛粪有机肥样品。

1.2 有机肥基本性状分析方法

采用《有机肥料》(NY 525—2012)对有机肥样品中有机质、氮、磷和钾等的测定方法进行检测。

1.3 有机肥中雌激素检测方法

采用SPE-HPLC/FLD法^[19-20]检测有机肥中雌激素含量。称取冷冻干燥并经粉碎机粉碎后过20目筛的(1.00 $\pm$ 0.01)g有机肥样品,加入1.00 mL的雌激素(空白组加入等量的甲醇)混合标准溶液(1 mg $\cdot$ L⁻¹),混合均匀后放置12 h,再加入20 mL提取剂(乙酸乙酯),涡旋30 s后超声提取1 h,并以4000 r $\cdot$ min⁻¹离心30 min,取5 mL上清液通过C18固相萃取柱,用15.00 mL体积比为1:1的甲醇和乙酸乙酯混合液洗脱,洗脱液收集至小试管中。将小试管置于40℃的恒温水浴并用氮气缓慢吹干,然后加入甲醇溶液涡旋混合,将附着物重新溶解至2.00 mL,过0.22 μ m孔径滤膜后,HPLC/FLD分析。色谱条件:色谱柱为Inertsil ODS-SP-C18(150 mm $\times$ 4.6 mm, 5 μ m);流动相为甲醇/乙腈/水(体积比为20:30:50);流速1.00 mL $\cdot$ min⁻¹;柱温40℃;进样量20 μ L;荧光检测器采用波长切换,切换方式如下,0~5.2 min激发/发射波长为300/450 nm, 5.2~7.1 min激发/发射波长为280/310 nm, 6.1~10.4 min激发/发射波长为300/450 nm, 10.4 min~25.0 min激发/发射波长为280/310 nm。

2 结果与讨论

2.1 有机肥的基本性状

不同畜禽粪便有机肥中主要营养物质含量如表1所示。鸡粪有机肥、猪粪有机肥和牛粪有机肥中有机质均值分别为54.17%、59.02%和46.57%;N均值分别为1.85%、1.58%和1.55%;P₂O₅均值分别为7.96%、11.13%和7.52%;K₂O均值分别为2.10%、1.39%和2.34%。从表1可知,所收集的17种有机肥样品绝大部分都满足《有机肥料》(NY 525—2012)中对有机肥的营养物质含量的要求:有机质 $\geq$ 45%,总养分(N+

表1 畜禽粪便有机肥中主要营养物质含量(%)

Table 1 Main nutrients content in organic fertilizers from livestock manures (%)

种类 Type of organic fertilizer	编号 Number	有机质 Organic matter	N	P ₂ O ₅	K ₂ O
鸡粪有机肥	YH1	61.22±0.41	2.56±0.02	7.35±0.04	2.42±0.06
	YH2	54.02±0.26	2.07±0.05	8.11±0.02	0.69±0.01
	YH3	75.09±0.33	1.48±0.03	7.51±0.12	1.23±0.06
	YH4	58.45±0.52	0.99±0.01	2.40±0.01	3.87±0.08
	YH5	40.87±0.30	1.56±0.02	12.09±0.14	0.65±0.01
	YH6	66.87±0.53	2.02±0.03	6.41±0.08	1.51±0.05
	YH7	43.96±0.66	0.98±0.01	8.79±0.10	4.39±0.02
	YH8	40.98±0.33	2.35±0.05	16.51±0.14	1.87±0.01
	YH9	47.91±0.23	2.66±0.01	2.40±0.01	2.25±0.02
猪粪有机肥	YS1	76.00±0.35	1.57±0.01	11.50±0.09	1.02±0.02
	YS2	65.93±0.45	1.83±0.03	5.52±0.15	2.35±0.08
	YS3	37.92±0.62	1.27±0.05	14.36±0.12	1.63±0.06
	YS4	56.22±0.27	1.64±0.02	13.12±0.03	0.58±0.02
牛粪有机肥	YC1	55.85±0.42	2.11±0.02	4.21±0.01	3.01±0.04
	YC2	45.37±0.62	0.89±0.01	5.36±0.05	1.53±0.05
	YC3	38.99±0.63	2.12±0.04	8.18±0.02	2.46±0.02
	YC4	46.05±0.82	1.08±0.01	12.32±0.22	2.35±0.09

注:YH1~9表示鸡粪有机肥;YS1~4表示猪粪有机肥;YC1~4表示牛粪有机肥。下同。

Note: YH1~9 represent organic fertilizers derived from chicken manures; YS1~4 represent organic fertilizers derived from swine manures; YC1~4 represent organic fertilizers derived from cow manures. The same below.

P₂O₅+K₂O)≥5.0%。但有机肥样品中的鸡粪样品YH5、YH7、YH8,猪粪样品YS3以及牛粪样品YC3中有机质含量低于标准,未能达到有机肥质量要求,需要加强质量监管力度。

2.2 有机肥中雌激素的含量

各种脊椎动物雌激素的排放种类和排放量因动物种类、生长阶段、年龄和性别差异而不同^[21-22],本文选择了普遍存在的天然雌激素E3、17β-E2以及合成雌激素BPA、EE2进行研究。采用SPE-HPLC/FLD法对有机肥样品中E3、17β-E2、BPA和EE2进行检测,结果如表2所示。有机肥样品YH2、YH5、YH7、YH9、YS1、YS4、YC2、YC3、YC4未检测到雌激素,其余8个有机肥样品均有不同含量的雌激素被检出。有机肥中雌激素含量范围和均值如表3所示,E3、17β-E2、BPA和EE2的含量(干质量计)范围分别为ND~2 417.34、ND~167.34、ND~514.91 μg·kg⁻¹和ND~186.97 μg·kg⁻¹。E3、17β-E2、BPA和EE2的均值(干质量计)分别为298.52、11.28、54.24 μg·kg⁻¹和11.00 μg·kg⁻¹。说明市场上畜禽粪便有机肥中部分产品含有雌激素,并且含量较高,这种产品施加到农田土壤将造成一系列安全隐患。所以,在售卖、使用畜禽粪便有机肥前,应对雌激素进行检测,并制定安全标准。而四种雌激素中E3的含量远高于

17β-E2、BPA和EE2三种雌激素,表明有机肥中E3相对于其余三种雌激素存在较大的污染风险。因此对于畜禽有机肥需重视E3的潜在污染风险,同时不能忽视17β-E2、BPA和EE2的污染风险。

2.3 有机肥与畜禽粪便中雌激素的对比

将鸡粪、猪粪、牛粪有机肥中雌激素与此前研究^[11]中新鲜鸡粪、猪粪、牛粪中雌激素(表4)进行比较。此前研究所用新鲜鸡粪、猪粪、牛粪样品采自南京附近各处养殖场,而本研究收集有机肥并不是由这些新鲜粪便制备。所以,有机肥中E3(298.52 μg·kg⁻¹)、17β-E2(11.28 μg·kg⁻¹)、BPA(54.24 μg·kg⁻¹)、EE2(11.00 μg·kg⁻¹)含量并未表现出明显比新鲜粪便中E3(218.95 μg·kg⁻¹)、17β-E2(42.83 μg·kg⁻¹)、BPA(43.44 μg·kg⁻¹)、EE2(19.84 μg·kg⁻¹)含量低的现象,而检出率相对于含量更具有对比意义。有机肥和新鲜粪便中雌激素检出率如图1所示,鸡粪、猪粪、牛粪有机肥中四种雌激素的检出率均明显低于对应新鲜粪便。所有有机肥中E3、17β-E2、BPA、EE2检出率分别为47.06%、11.76%、17.65%、5.88%,而新鲜粪便中E3、17β-E2、BPA、EE2检出率则分别高达67.74%、70.97%、70.97%、58.06%,说明将新鲜粪便通过堆肥发酵制备有机肥能够使雌激素发生降解而含量降

表2 有机肥中雌激素含量($\mu\text{g}\cdot\text{kg}^{-1}$)Table 2 The concentration of estrogens in organic fertilizers($\mu\text{g}\cdot\text{kg}^{-1}$)

编号 Number	E3	17 β -E2	BPA	EE2
YH1	528.48 $\pm$ 75.58	ND	ND	ND
YH2	ND	ND	ND	ND
YH3	784.36 $\pm$ 188.76	24.43 $\pm$ 6.92	276.44 $\pm$ 67.12	ND
YH4	575.22 $\pm$ 99.22	ND	514.91 $\pm$ 195.13	ND
YH5	ND	ND	ND	ND
YH6	270.00 $\pm$ 42.74	ND	ND	ND
YH7	ND	ND	ND	ND
YH8	274.08 $\pm$ 17.29	ND	ND	ND
YH9	ND	ND	ND	ND
YS1	ND	ND	ND	ND
YS2	2 417.34 $\pm$ 232.20	167.34 $\pm$ 73.34	ND	186.97 $\pm$ 49.69
YS3	21.51 $\pm$ 1.02	ND	130.74 $\pm$ 16.53	ND
YS4	ND	ND	ND	ND
YC1	203.85 $\pm$ 56.29	ND	ND	ND
YC2	ND	ND	ND	ND
YC3	ND	ND	ND	ND
YC4	ND	ND	ND	ND

注:ND表示未检出或低于检出限。下同。

Note:ND represent not detected or under detection limit. The same below.

表3 有机肥中雌激素含量和均值($\mu\text{g}\cdot\text{kg}^{-1}$)Table 3 The concentration range and mean concentration of estrogens in the organic fertilizers($\mu\text{g}\cdot\text{kg}^{-1}$)

种类 Types	项目 Items	E3	17 β -E2	BPA	EE2
鸡粪有机肥 ($n=9$)	含量范围	ND~784.36	ND~24.43	ND~514.91	ND
	均值	270.22	2.71	87.93	0
猪粪有机肥 ($n=4$)	含量范围	ND~2 417.34	ND~167.34	ND~130.74	ND~186.97
	均值	609.71	41.84	32.69	46.74
牛粪有机肥 ($n=4$)	含量范围	ND~203.84	ND	ND	ND
	均值	50.96	0	0	0
总计($n=17$)	含量范围	ND~2 417.34	ND~167.34	ND~514.91	ND~186.97
	均值	298.52	11.28	54.24	11.00

表4 新鲜鸡粪、猪粪、牛粪中雌激素的含量^[11]($\mu\text{g}\cdot\text{kg}^{-1}$)Table 4 The concentration of estrogens in chicken, swine and cow fresh manures^[11]($\mu\text{g}\cdot\text{kg}^{-1}$)

种类 Types	项目 Items	E3	17 β -E2	BPA	EE2
新鲜鸡粪 ($n=12$)	含量范围	ND~1 764.32	ND~227.06	ND~166.52	ND~67.51
	均值	289.84	38.62	63.59	14.28
新鲜猪粪 ($n=9$)	含量范围	174.22~518.16	ND~201.30	ND~361.82	ND~70.11
	均值	330.30	52.88	51.87	25.10
新鲜牛粪 ($n=10$)	含量范围	ND~240.92	ND~88.28	ND~33.31	ND~106.28
	均值	33.68	38.82	11.66	21.78
总计($n=31$)	含量范围	ND~1 764.32	ND~227.06	ND~361.82	ND~106.28
	均值	218.95	42.83	43.44	19.84

低^[12,23]。但有机肥中雌激素检出率仍然较高,所以目前所用堆肥发酵制备有机肥工艺仍需改进。此外,牛

粪新鲜粪便中雌激素含量和检出率相对鸡粪、猪粪较低,制备的有机肥中雌激素较易降解完全,所以牛粪

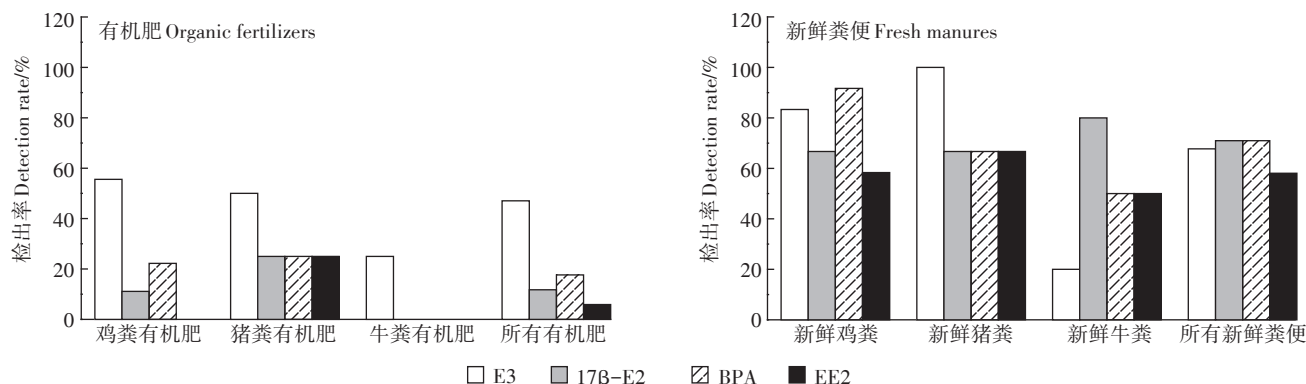


图1 有机肥和新鲜粪便中雌激素检出率

Figure 1 Detection rate of estrogens in organic fertilizers and fresh manures

有机肥中雌激素含量和检测率非常低。牛粪有机肥相对鸡粪、猪粪有机肥污染风险更小,更能满足环境保护的需要。

3 结论

(1)对采集的有机肥样品中有机质、全氮、全磷、全钾进行检测,发现并不是所有产品都能达到《有机肥料》(NY 525—2012)中对有机肥营养物质含量的要求。

(2)对采集的有机肥样品中雌激素进行检测,发现市场上畜禽粪便有机肥中部分产品含有雌激素,且含量较高,其中E3的含量远高于17β-E2、BPA和EE2,存在较大的污染风险。

(3)将有机肥中雌激素与新鲜畜禽粪便中雌激素进行对比,发现有机肥中四种雌激素检出率均明显较低,说明将新鲜粪便通过堆肥发酵制成有机肥能够使雌激素发生降解,从而降低污染风险,但有机肥中雌激素检出率仍然较高。此外,三种粪便制备的有机肥中,牛粪有机肥中雌激素含量和检出率更低,较为安全。

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