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西藏自治区隆子县土壤硒地球化学特征及影响因素

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摘要: 硒是人体必需的微量元素之一,土壤中的硒含量与人体健康关系密切。调查土壤硒含量分布特征、圈定富硒土壤资源分布区、查明土壤硒含量影响因素,对于推动富硒土地资源开发利用、发展富硒农牧产业、预防地方疾病等均具有重要意义,也可为土壤硒背景值研究提供参比资料。土壤硒是当前热点研究领域,国内外对土壤硒研究已有很多,然而西藏地区有关土壤硒方面研究资料非常有限。本文选择西藏自治区隆子县重点耕地区为研究对象,系统采集表层土壤、垂向剖面、岩石样等样品,采用原子荧光光谱法(AFS)、容量法(VOC)、电感耦合等离子体发射光谱法(ICP-OES)等方法测定土壤中的硒、有效硒、有机质、全磷等含量指标,利用统计方法对研究区土壤硒、有效硒等地球化学含量特征及影响因素进行初步探讨。结果表明:①研究区表层土壤硒含量范围为 0.14~1.51mg/kg,中位数为 0.44mg/kg,是西藏土壤硒平均值(0.15 mg/kg)的 2.9 倍和中国表层土壤 Se 平均值(0.26mg/kg)的 1.5 倍,表明研究区表层土壤中全硒含量较高;研究区表层土壤中有效硒含量范围为 0.8~26.8μg/kg,中位数为 9.2μg/kg,土壤有效硒占全硒含量的 0.21%~5.79%;土壤硒含量高于 0.4mg/kg 为界限值,研究区总面积的 77.25%符合富硒土壤划定标准,表明富硒土壤资源丰富;②研究区广泛分布的涅如组(T_3n)和日当组(J_1r)地层发育土壤中硒含量较高,中位数分别为 0.44mg/kg 和 0.41mg/kg,土壤硒含量与地质背景密切相关;土壤理化性质包括有机质、pH、TFe_2O_3 等对土壤全硒含量影响不显著,但土壤有效硒与有机质、pH、N、P、碱解氮、有效磷、速效钾、阳离子交换量(CEC)呈显著正相关;此外,铁氧化物(TFe_2O_3)对有效硒含量也有一定控制作用;③土壤垂向剖面研究发现,土壤硒含量还与表生富集作用有关。综合认为,研究区土壤 Se 含量较高,富硒土壤资源丰富,可以通过土壤养分管理,进一步提高土壤硒生物有效性。

关键词: 土壤硒; 地球化学特征; 影响因素; 原子荧光光谱法; 西藏隆子县

要点:

(1) 研究区土壤 Se 含量范围为 0.14~1.51mg/kg,中位数为 0.44mg/kg,明显高于西藏和中国表层土壤硒含量平均值。

(2) 土壤硒含量与地质背景密切相关,受涅如组和日当组黑色岩系控制。

(3) 土壤有机质、N、P、碱解氮、有效磷、速效钾、CEC 含量对土壤有效性产生影响。

中图分类号: S151.93; O657.31　　**文献标识码:** A

硒(Se)是人体和动物必需的微量元素之一。国内外大量研究表明,硒元素对人体具有多种生物学功能,包括抗氧化、免疫力调节、拮抗等作用[1];研究还表明,人体对硒的需求范围很窄,硒摄入量不

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足会引起癌症、肝病、大骨节病等一系列疾病,而硒摄入过量也会引起硒中毒[2-3]。因此,中国营养学会制定出成人推荐硒日摄入量为50~400μg。人体或动物体内的微量元素硒不能通过自身合成,只能从外界食物中补充;食物中硒,特别是植物性食物中的硒主要来自于土壤,因此,土壤中的硒与人体健康关系密切。从全球来看,土壤缺硒现象非常普遍,据估计,全世界约有15%人口缺乏硒元素[4]。中国是世界上硒缺乏最严重的国家之一,从东北三省至云贵高原存在一条低硒带,约占国土面积的72%,其中30%为严重缺硒地区[5],而西藏也在这条低硒带上,目前该低硒带的成因至今仍不明确。有研究者认为,中国土壤低硒带与气候成因有关[6-7]。最近研究表明,中国大约有51%的土壤缺硒[8];也有研究表明,中国土壤总体上不缺硒,但贫硒国土面积仍占30%左右[9]。根据中国多目标地球化学调查成果显示,全国表层土壤硒平均值0.217mg/kg,约有33.34%的土壤硒潜在不足和缺硒[10]。近年来,全国各地陆续开展了土地质量地球化学调查工作,也发现大量的富硒土壤资源,有效支撑服务了脱贫攻坚及乡村振兴。因此,土壤硒研究也成为地学行业的热点研究内容之一。

西藏是青藏高原主体部分,拥有复杂多样的成土母质和成土过程,形成了独特的高山土壤类型;此外,西藏地区是人类活动影响最少的地区之一,是环境地球化学研究最理想场所。然而,受自然地理位置和气候等诸多因素影响,在西藏地区有关土壤元素地球化学方面研究资料非常有限,尤其是有关土壤和植物硒方面研究甚少。目前主要成果有国家“七五”攻关课题涉及的西藏土壤环境背景值调查,发现西藏地区95%的土壤Se含量在0.049~0.365mg/kg之间,平均值为0.15mg/kg[11]($n=205$件),西藏土壤硒含量显著低于中国表层土壤硒水平[12],此后土壤硒相关研究只集中在少数几个县,未涉及整个西藏的系统研究,故目前西藏地区土壤背景值数据均来自于该调查结果。曲航等[13]对西藏青稞主产区土壤和籽粒硒含量调查发现,土壤全硒平均值为0.18mg/kg($n=80$件),青稞籽粒硒平均值为0.011mg/kg($n=67$件);次仁旺堆等[14]研究发现,西藏乃东区土壤硒含量范围为0.08~0.71mg/kg,平均值为0.23mg/kg($n=1022$件),特别是雅江北部土壤中硒平均含量仅为0.14mg/kg;此外,也有研究者对土壤-青稞系统中硒的转运规律研究发现,植物对硒的吸收限制因素为植物根系[15]。可以看出,西藏土壤整体上缺硒是不可争辩的事实,但西藏地域辽阔,拥有复杂多样的成土母质和成土过程,仅少量样点来评价整个西藏土壤硒状况,势必会影响最终结果。此外,大量研究表明,土壤Se含量受成土母质、土地利用方式、土壤理化性质等多种因素不同程度的影响[16-19],不同区域影响程度存在一定的差异。刘才泽等[20]、武芝亮等[21]研究认为,土壤硒含量与黑色岩系有关,受成土母质控制;曹容浩[17]、郭军等[18]研究认为,土壤硒含量受有机质、pH值等显著影响。了解土壤中硒和有效硒含量及影响因素,对富硒土壤资源开发利用具有重要意义。

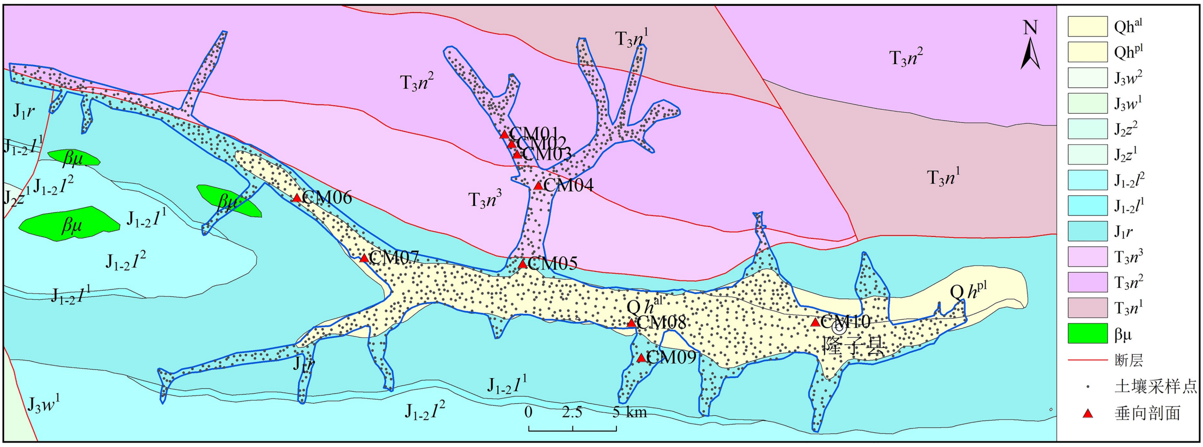
本文以西藏自治区隆子县重点耕地区为研究对象,系统采集表层土壤、垂向剖面、岩石剖面等样品,采用原子荧光光谱法(AFS)、电感耦合等离子体发射光谱法(ICP-OES)、容量法(VOL)等方法测定Se、有效硒、有机质等指标。利用数理统计分析、GIS软件等方法,讨论研究区土壤硒含量特征、分布及影响因素,以期为高原边疆民族地区富硒土地资源的开发利用提供依据。

1 研究区概况

研究区位于西藏自治区山南市隆子县,地处喜玛拉雅山北麓的藏南谷地,该区属于高原半干旱大陆性季风气候。研究区地貌主要是高原宽谷地貌,谷底一般3~8km,最宽达15km,阶地和洪积扇发育,光温水资源充足。研究区土壤类型主要为高山土-棕冷钙土类。研究区土地利用类型主要以农用地为主,其中耕地和草地比重较大。研究区出露的地层为:三叠系上统涅如组(T_3n)、侏罗系下统日当组(J_1r)、侏罗系中下统陆热组($J_{1-2}l$)和第四系(Qh),其中涅如组和日当组地层为研究区出露的主要地层,其主要岩性分别为粉砂质(绢云母)板岩和页岩或粉砂岩(图1)。

2 样品采集方法

研究区面积为200km^2,采集表层土壤样品1587件(图1),实际分析样品1587件。野外采样时以实际地块形状来确定采样方法,当地块为正方形时,采用“X”型采样,当地块长方形时,采用“S”型采样。具体采样方法及样品加工按照《土地质量地球化学评价规范》(DZ/T 0295—2016)规范要求执行。耕地采样时,由5个子样点等量组合而成1件样品;草地、林地等采样时,由3~4个子样点等量组合而成1件样品。将各子样点采集的样品揉碎,挑出小石块、根系等杂物,充分混合后,用四分法留取1000g以上样品装入样袋。为了研究硒元素在土壤垂直方



Qh^{al}—第四系冲积物；Qh^{pl}—第四系洪积物；J_3w^2—维美组二段；J_3w^1—维美组一段；J_2z^2—遮拉组二段；J_2z^1—遮拉组一段；$J_{1-2}l^2$—陆热组二段；$J_{1-2}l^1$—陆热组一段；J_1r—日当组；T_3n^3—涅如组三段；T_3n^2—涅如组二段；T_3n^1—涅如组一段；βμ—辉绿岩脉。

图 1　研究区地质简图及采样点位图

Fig. 1　Geological sketch and sampling point map of the study area. The black dots represent the topsoil sampling sites, the red triangles represent the vertical profile locations, and the blue lines represent the study area.

向上的分布和迁移特征，在研究区不同区域施工 10 条土壤垂向剖面，剖面编号为 CM01 至 CM10（图 1），除 CM01 剖面深度 140cm 外，其余剖面深度均为 160cm，剖面样从深部至表层每 20cm 采集一件样品，共计采集 78 件土壤剖面样品。样品加工严格按照相关规范要求执行，过筛后正样质量保证在 200g 以上，并及时进行送样分析测试。涅如组二段地层中测量一条岩石剖面，采集岩石样品 15 件。在研究区不同区域采集的 130 件样品进行阳离子交换量（CEC）分析。

3　样品分析测试及质量控制

3.1　样品分析测试

本次所采集的土壤和岩石样品分析测试工作均由湖北省地质实验测试中心完成，严格按照《土地质量地球化学评价规范》（DZ/T 0295—2016）、《生态地球化学评价样品分析技术要求（试行）》（DD2005-03）等地质行业的相关规范要求执行。表层土壤样品分析了 Se、有效硒、有机质、pH、N、P、碱解氮、速效磷、速效钾等指标，各指标分析方法及检出限见表1，可见本次所采用分析方法的检出限

表 1　土壤样品分析方法及检出限

Table 1　Analytical methods and detection limit for soil samples

分析指标	分析方法	样品处理方法	检出限要求（mg/kg）	检出限（mg/kg）	方法依据
Se	原子荧光光谱法（AFS）	王水加热消解，盐酸浸提	0.01	0.01	WHCS-FF-CS/04—2019
有效硒	原子荧光光谱法（AFS）	沸水浸取	-	0.0005	WHCS-FF-CS/22—2019
有机质	容量法（VOL）	浓硫酸加热消解	0.17	0.034	NY/T 1121.6—2006
pH	离子选择性电极法（ISE）	无二氧化碳水浸取	0.1	0.1*	WHCS-FF-CS/19—2019
TFe_2O_3	电感耦合等离子体发射光谱法（ICP-OES）	四酸加热消解，盐酸浸提	0.05	0.02	WHCS-FF-CS/02—2019
N	元素分析仪法（EA）	固体燃烧	20	15	WHCS-FF-CS/12—2019
P	电感耦合等离子体发射光谱法（ICP-OES）	粉末压片	10	4.3	WHCS-FF-CS/02—2019
碱解氮	容量法（VOL）	碱解-扩散	-	1	LY/T 1228—2015
速效磷	电感耦合等离子体发射光谱法（ICP-OES）	中碱性：碳酸氢钠浸取； 酸性：氟化铵-盐酸浸取	0.25	0.2	LY/T 1232—2015
速效钾	电感耦合等离子体发射光谱法（ICP-OES）	乙酸铵浸取	1.25	1	LY/T 1234—2015
阳离子交换量（CEC）	容量法（VOL）	乙酸铵浸取	2.5	1**	LY/T 1243—1999

注：“*”单位为无量纲；“**”单位为 cmol/kg；“-”无检出限值。

优于规范中检出限要求,能满足研究区样品分析要求。

鉴于目前土壤有效硒含量测试还没有统一的分析方法,本次采用的土壤有效硒测试方法为:称取 10.0g 样品于 50mL 烧杯中,加入 20mL 沸水,摇匀后置于 160℃ 电热板上加热,10min 后取下,冷却后过滤,取 5mL 滤液于聚四氟乙烯烧杯中,加硝酸和过氧化氢,于 100℃电热板蒸至小体积后,加 50%盐酸后加热还原,转移至比色管中,采用 AFS 测定有效硒含量。

3.2 分析数据质量控制

本次表层土壤样品分析过程中,共插入 37 件重复样品,重复样合格率 100%;共插入 12 个国家一级标准物质对分析测试结果的准确度、精确度、报出率等进行内部质量监控,结果表明样品的准确度和精密度及报出率均符合规范要求,总合格率为 100%;共抽取 112 件样品做重复性检验分析,重复性检验总合格率均大于 96.36%,符合规范要求。岩石样分析过程中,共插入国家一级标准物质 3 件,合格率为 100%;抽取 2 件样品重复性检验,合格率为 100%,报出率为 100%。研究区所有样品分析测试由专家组进行分析质量验收,各项质量指标均达到了相关的规范要求,样品分析数据质量可靠。

4 结果与讨论

4.1 土壤硒地球化学特征

4.1.1 表层土壤硒地球化学特征

研究区原始分析数据和均值加减 3 倍标准差剔除离群值后,对数据进行正态分布检验发现,硒和有效硒含量均不服从正态分布,因此,以中位数作为研究区背景值。从统计结果(表 2)可以看出,研究区表层土壤硒含量范围为 0.14~1.51mg/kg,中位数为 0.44mg/kg,是西藏土壤硒平均值(0.15mg/kg)[11-12]的 2.9 倍和中国表层土壤(0~20cm)硒平均值(0.26mg/kg)[22]的 1.5 倍,表明研究区表层土壤硒含量较高。硒元素变异系数为 0.23,表明研究区表层土壤硒含量分布相对均匀。

土壤有效硒含量高低直接影响着植物中硒的含量水平,在研究区表层土壤中有效硒含量范围为 0.8~26.8μg/kg,中位数为 9.2μg/kg,占土壤全硒含量的 0.21%~5.79%之间,平均值为 2.11%,低于安徽宁国市[23]、海南[24]表层土壤有效硒含量。研究区土壤硒与有效硒含量进行相关性分析,两者指标之间具有一定的相关性($R=0.183$, $P<0.01$),表明土壤中随着全硒含量增加而有效硒含量也有所提高。

按照谭见安的《中华人民共和国地方病与环境图集》[5]中硒等级划分标准,对研究区土壤硒含量进行等级划分,利用土地质量地球化学调查与评价数据管理与维护(应用)子系统软件绘制研究区土壤硒含量空间分布图(图 2)。可见,研究区总面积的 77.25%土壤达到富硒土壤标准,主要分布在隆子镇和日当镇,研究区不存在土壤硒不足和硒中毒,表明研究区富硒土壤资源丰富,且集中连片分布(图 2),具有富硒土壤开发潜力。

4.1.2 土壤垂向剖面硒含量特征

根据 10 条垂向剖面分析结果显示,从表层至深部土壤中全硒含量中位数分别为 0.44mg/kg(0~20cm)、0.46mg/kg(20~40cm)、0.46mg/kg(40~

表 2 表层土壤地球化学参数特征

Table 2 Characteristics of geochemical parameters for surface soil

分析指标	最小值	最大值	平均值	中位数	标准离差	变化系数
Se(mg/kg)	0.14	1.51	0.45	0.44	0.10	0.23
有效硒(μg/kg)	0.79	26.80	9.20	8.80	3.56	0.39
有机质(%)	0.37	10.50	2.53	2.45	1.03	0.41
pH	5.81	8.86	8.22	8.32	0.41	0.05
TFe_2O_3(%)	3.53	14.00	7.06	6.88	0.99	0.14
N(mg/kg)	489.00	4412.00	1822.81	1792.00	571.10	0.31
P(mg/kg)	289.00	1728.00	839.03	832.00	193.97	0.23
碱解氮(mg/kg)	10.00	472.00	100.99	93.80	49.61	0.49
速效磷(mg/kg)	0.66	94.30	10.96	7.51	10.00	0.91
速效钾(mg/kg)	6.00	794.00	111.15	80.00	89.00	0.80
西藏土壤硒(mg/kg)	0.04	0.37	0.15	0.14	/	0.48
中国表层土壤硒(mg/kg)	0.00	49.60	0.26	0.21	0.22	0.80

注:西藏土壤硒含量数据引自《西藏土壤元素背景值及其分布特征》(成廷鳌等,1993);中国表层土壤硒含量数据引自《中国土壤地球化学参数》(侯青叶等,2020)。

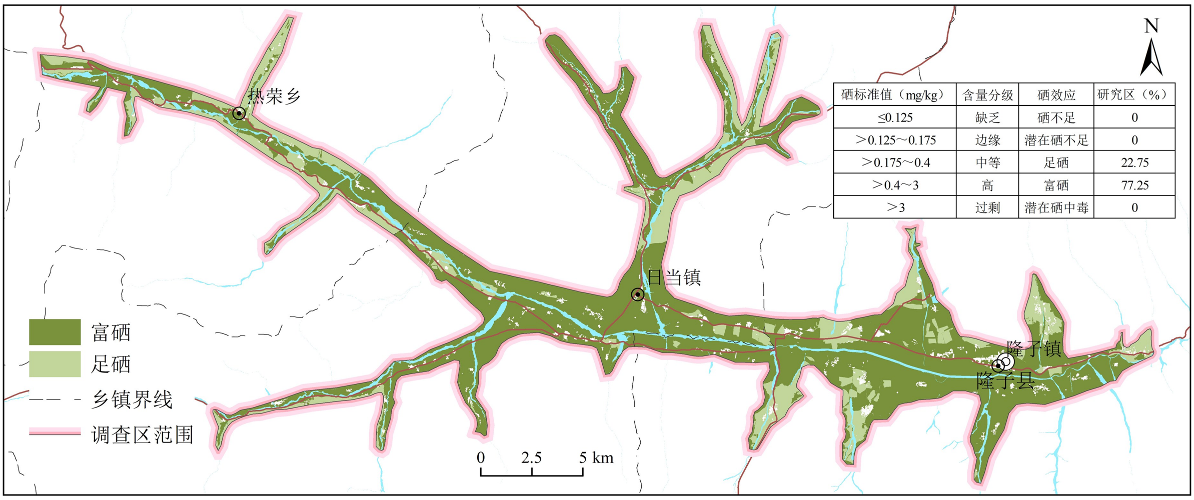


图 2　研究区表层土壤硒空间分布图

Fig. 2　Spatial distribution characteristics of topsoil selenium concentration in the study area. Dark green represents the selenium-enriched soil, which accounts for 77.25% of the total area of the study area; the light green color represents the soil with sufficient selenium, which accounts for 22.75% of the total area of the study area.

60cm)、0.43mg/kg(60~80cm)、0.40mg/kg(80~100cm)、0.37mg/kg(100~120cm)、0.33mg/kg(120~140cm)、0.34mg/kg(140~160cm)。可以看出,深度 20~60cm 处土壤中硒含量最高,随着剖面深度加深,土壤全硒含量逐渐减少,剖面深度约 1m 以下全硒含量小于 0.4mg/kg,表明土壤硒含量可能受淋溶或生物积累作用导致土壤浅层富集[25]。从垂向剖面土壤硒含量变化趋势(图 3)可以看出,剖面 CM02、CM03、CM04 号从深部至表层硒含量逐渐增加,属于表聚型;其余的剖面均出现明显拐点,其中剖面 CM01 在 20~40cm 处出现硒高值,剖面 CM05 在 100~140cm 处出现硒高值,剖面 CM06、CM09、CM10 在 60~80cm 处出现硒高值,剖面 CM07、CM08 在 40~60cm 处出现硒高值。总体来看,研究区土壤硒含量随着剖面深度增加而逐渐降低,这与较多研究者认为土壤中硒主要富集于较浅土壤中的结论基本相似[26-27]。

土壤垂向剖面中有效硒含量也随着剖面深度增加而逐渐降低,在表层土壤中(0~20cm)有效硒中位数为 10.20μg/kg,深部土壤中(140~160cm)有效硒中位数仅 4.02μg/kg。可见,深部有效硒含量减少近 60%,表明表生环境下,土壤硒在淋溶或生物累积作用可以显著提高土壤硒的生物有效性,有利于植物对硒的吸收。

4.2　土壤硒含量影响因素

土壤硒含量受成土母质、土壤类型、土地利用类型、理化性质、人为因素等多种因素的综合影响。本文为了研究土壤硒和有效硒含量的影响因素,选择成土母质、土地利用类型、土壤基本理化性质等因素,探讨土壤硒和有效硒与各因素之间的相关关系。

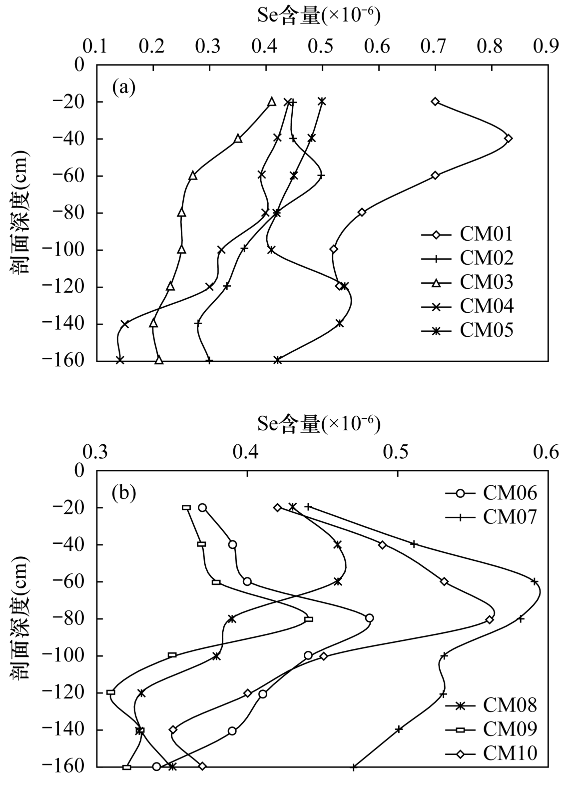


图 3　土壤垂向剖面硒含量特征

Fig. 3　Soil vertical profile Se content characteristics. The abscissa represents the soil Se content and the ordinate represents the profile depth. The content of Se in soil decreases with the increase of soil depth.

4.2.1　成土母质

成土母质是土壤形成的物质基础，也是土壤中硒的主要来源。研究表明，不同岩石中硒含量差异明显，在三大岩类中硒含量大小依次为：变质岩>火成岩>沉积岩[28]。研究区出露的地层相对单一，大致以隆子河谷为界，以南出露地层为日当组和陆热组地层，以北出露地层为涅如组地层，隆子河谷流域为第四系冲(洪)积物。研究区土壤硒高背景主要与成土母质有关，在涅如组(T_3n)和日当组(J_1r)地层发育土壤中硒含量平均值较高(表 3)，该两组地层发育土壤中硒含量高于 0.4mg/kg 的样品数有 854 件，占样品总数的 68.44%。

值得一提的是，陆热组地层发育土壤中硒含量也高，但该地层在研究区分布面积十分有限，仅有 8 件表层土壤样品，因此该地层不是主要土壤硒来源。研究区北部为西藏乃东区，将该两地区主要地层发育土壤硒含量进行对比发现，研究区涅如组和日当组地层发育土壤中硒含量显著高于乃东区宋热岩组、比马组和典中组地层。

为了进一步了解土壤硒来源，在研究区北部涅如组二段地层中测量一条岩石剖面，经岩石样品分析，岩石中硒含量范围为 0.07~11.00mg/kg，平均值为 1.65mg/kg，硒高值点主要分布于绢云母板岩和页岩中，也进一步证实了研究区土壤硒主要来源为成土母岩，这与许多研究者在不同地区调查发现土壤硒与黑色岩系密切相关结论一致[29-31]。

4.2.2　土地利用类型

土地利用对硒生物地球化学的影响可以被潜在的地质条件所调节[32]。一些研究者认为，硒含量在不同用地类型条件下存在显著差异[33-34]。研究区土地利用类型主要为水浇地、天然牧草地、灌木林地和人工牧草地。

表 3　研究区不同地层分布区土壤中硒参数统计

Table 3　Statistics of selenium parameters in soils of different stratigraphic distribution areas in the study area

地层	样品数量	硒含量最小值(mg/kg)	硒含量最大值(mg/kg)	硒含量算术平均值(mg/kg)	硒含量中位数(mg/kg)	标准差(mg/kg)	变异系数
涅如组三段(T_3n^3)	110	0.22	1.03	0.43	0.42	0.11	0.25
涅如组二段(T_3n^2)	317	0.22	1.51	0.46	0.44	0.14	0.31
涅如组一段(T_3n^1)	28	0.24	0.77	0.47	0.45	0.12	0.26
日当组(J_1r)	401	0.14	1.35	0.43	0.41	0.11	0.27
陆热组($J_{1-2}l$)	8	0.28	0.73	0.50	0.49	0.15	0.31
第四系(Qh)	711	0.14	0.72	0.45	0.45	0.07	0.15
辉绿岩(βμ)	9	0.14	0.46	0.37	0.44	0.11	0.30
花岗斑岩(γπ)	3	0.39	0.49	0.45	0.48	0.06	0.12
比马组(K_1b)*	23	0.08	0.22	0.12	0.12	0.03	0.23
宋热岩组(T_3s)*	78	0.15	0.71	0.34	0.29	0.13	0.40
典中组(E_1d)*	24	0.10	0.44	0.23	0.22	0.09	0.42

注："*"数据来源于西藏乃东区重点耕地区 1：5 万土地质量地球化学调查数据。

表 4　不同土地利用方式土壤硒地球化学参数

Table 4　Geochemical parameters of selenium concentration in soils with different land use types

用地类型	样品数量	硒含量最小值(mg/kg)	硒含量最大值(mg/kg)	硒含量算术平均值(mg/kg)	硒含量中位数(mg/kg)	标准差(mg/kg)	变异系数
水浇地	860	0.26	0.98	0.45	0.44	0.07	0.17
旱地	20	0.38	0.58	0.47	0.46	0.05	0.11
天然牧草地	424	0.14	1.51	0.43	0.41	0.16	0.37
人工牧草地	81	0.26	0.74	0.44	0.43	0.08	0.18
灌木林地	115	0.25	0.65	0.45	0.46	0.07	0.15
其他林地	37	0.33	0.63	0.46	0.45	0.09	0.18
乔木林地	40	0.32	0.55	0.45	0.45	0.05	0.11
沼泽草地	6	0.33	0.7	0.53	0.52	0.14	0.27
内陆滩涂	4	0.33	0.43	0.4	0.42	0.05	0.12

经统计(表 4),在沼泽草地土壤中硒含量明显高于其他用地类型,可能是沼泽草地土壤中富含腐植质,对硒有较强的吸附和络合能力,故土壤硒含量高;在灌木林地和旱地分布区表层土壤中硒含量稍微高,中位数均为 0.46mg/kg,在天然牧草地分布区表层土壤中硒的含量稍低,中位数为 0.41mg/kg,总体上,不同用地类型土壤中的硒含量差异不显著。

4.2.3 土壤理化性质

土壤理化性质包括有机质、pH 值、铁氧化物、大量养分元素、阳离子交换量(CEC),对土壤硒和有效硒的含量存在着不同程度的影响。

(1)有机质

有机质对土壤硒生物有效性具有双重作用:一方面有机质对表层土壤硒吸附固定作用,降低硒的生物有效性;另一方面有机质发生矿化后能释放出大量硒,从而增加土壤有效硒含量[35]。研究区土壤有机质含量范围值为 0.37%~10.5%,平均值为 2.53%。研究区 31.58%的土壤有机质含量较缺乏和缺乏。目前有机质与土壤硒含量之间的相关关系存在地域差异性,大部分研究者认为,土壤有机质和全硒或有效硒含量呈显著正相关[36-38]。将研究区土壤全硒含量与有机质含量进行相关性分析,结果两者之间并无显著相关。将土壤有机质含量与有效硒含量和有效硒/总硒比值进行相关性分析,土壤有机质含量与有效硒含量呈正相关($R^2=0.2792$, $P<0.01$)(图 4a),与有效硒/总硒比值之间也呈正相关性($R^2=0.2597$, $P<0.01$)(图 4b),说明土壤中有机质含量丰缺程度,直接影响着硒的生物有效性,通过提高土壤中有机质含量,可以有效地增加有效硒含量[39]。

(2)pH 值

pH 值是土壤硒的又一个重要控制因素,影响着土壤硒的形态和有效性。通常情况下,在碱性土壤硒主要以 SeO_4^{2-} 形式存在,生物有效性高,在中性和酸性土壤硒主要以 SeO_3^{2-} 形式存在,生物有效性相对较低[40-41]。研究区土壤 pH 范围为 5.81~8.6,平均值为 8.22。研究区 80.36%的土壤为碱性土壤(pH 7.5~8.5),12.72%为强碱性土壤(pH≥8.5),6.76%为中性土壤(pH 6.5~7.5),0.16%为酸性土壤(pH 5.0~6.5)。已有研究表明,土壤硒与 pH 值呈显著负相关[42-44];也有研究发现,当 pH≤7 时,pH 值与土壤硒呈正相关,pH>7 时,pH 值与土壤硒呈负相关[45]。说明不同 pH 值条件下,对土壤硒的

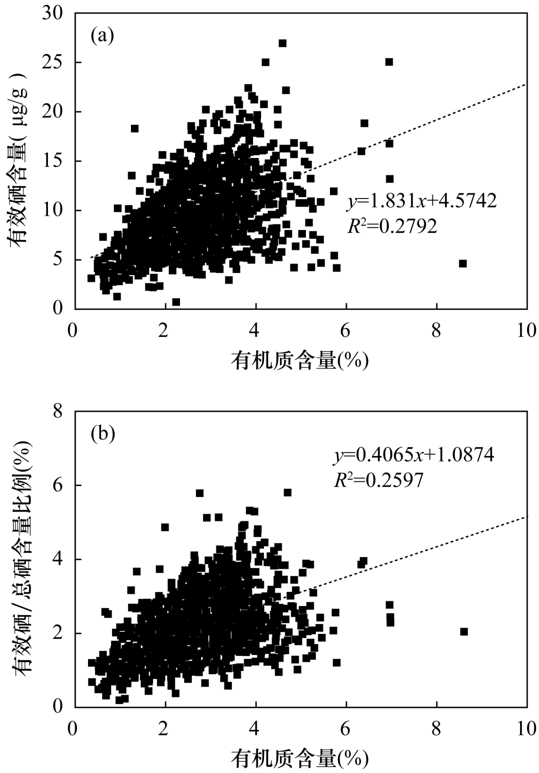


图 4　有机质含量与有效硒含量和有效硒/总硒比值散点图

Fig. 4　Scatter diagrams of organic matter content to available selenium and available selenium/total selenium ratio. (a) Correlation between organic matter and available selenium content; (b) Correlation between organic matter and the ratio of available selenium to total selenium. There is a positive correlation between soil organic matter content and available selenium content and the ratio of available selenium to total selenium. The dashed black line represents the trend line.

影响作用不一致。研究区土壤硒与 pH 值相关性分析发现,两者含量之间的相关性不显著,这与杨忠芳等[46]在海南岛农田土壤硒研究时发现,在碱性条件下土壤硒不受酸碱度(pH)制约,两者无明显相关性的结论基本一致。值得一提的是,虽然 pH 值与土壤硒之间并无显著相关性,但有效硒与 pH 值之间存在一定的正相关($R=0.103$, $P<0.01$)。研究区根据土壤 pH 分级标准,划分出酸性、中性、碱性和强碱性土壤,并分别计算不同分级标准中的有效硒和有效硒/总硒比值的平均值。土壤有效硒和有效硒/总硒比值在不同 pH 值的条件下,呈现规律性变化,土壤有效硒平均值分别为酸性(6.13μg/kg)、中性(6.32μg/kg)、碱性(9.72μg/kg)、强碱性(7.82μg/kg),可见在酸性土壤(pH 5.0~6.5)条件

下,硒的有效性相对较低,碱性土壤(pH 7.5~8.5)条件下土壤硒的有效性最高,而强碱性土壤(pH≥8.5)条件下,硒的有效性开始下降趋势,表明从酸性至碱性土壤硒的有效性逐渐增加,而强碱性条件下,可能硒甲基化反应,有效性开始降低[47]。

(3)铁氧化物

研究表明,不同 pH 值条件下,铁氧化物对表生环境硒的影响不一致,在酸性土壤条件下,土壤硒与铁氧化物(TFe_2O_3)呈显著正相关,表明氧化铁对硒有很强的吸附作用[48-49]。将研究区土壤铁氧化与硒含量进行相关性分析,两者之间并无显著相关性,但与有效硒含量之间存在一定的负相关($R=-0.346$,$P<0.01$)。由于研究区表层土壤以碱性土壤为主,TFe_2O_3 对硒的吸附能力低,这与徐文坡等[50]研究结果一致。

(4)大量养分元素

土壤中 N、P、K 等大量养分丰缺程度对人工调控土壤硒含量具有重要的理论意义,但目前对土壤硒或有效硒与大量养分之间关系的研究甚少。土壤有效硒与大量养分之间相关因子分析表明,研究区土壤有效硒与 N、P、碱解氮、速效磷、速效钾含量呈显著正相关性,说明随着 N、P、K 大量养分含量增加,可以显著地提高土壤硒的生物有效性(图 5 和表 5),这与余文权等[51]、吴正等[52]研究结果基本一致。

(5)阳离子交换量(CEC)

阳离子交换量(CEC)对土壤硒的生物有效性影响具有普遍性。本次研究区共采集 130 件表层土壤样品进行 CEC 分析,结果表明 CEC 含量范围为 6.94~16.92cmol/kg,CEC 与土壤全硒之间无显著相关性,但 CEC 与有效硒、有机质等呈显著的正相关(表 5),表明随着 CEC 含量增加,土壤有效硒的含量也增加[53],说明有机质含量是影响 CEC 的重要因素之一,这与前人在西藏第二次土壤普查资料中 CEC 专题研究结论基本一致[54]。

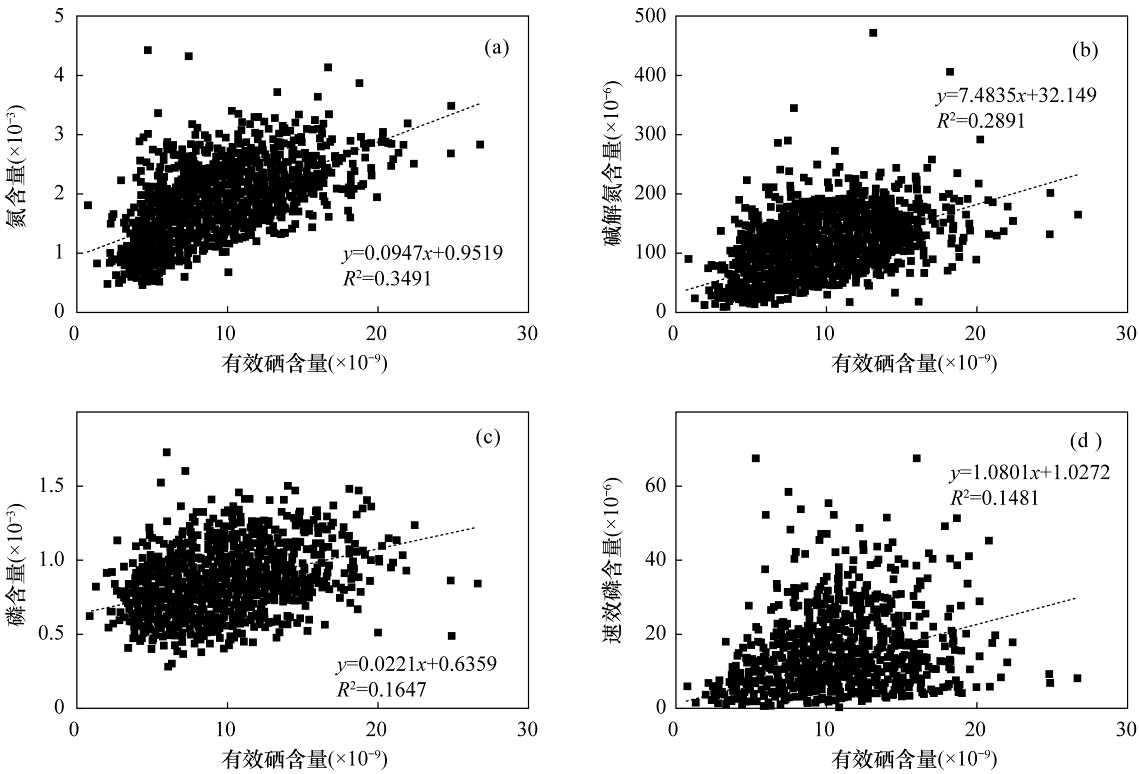


图 5 有效硒与(a) N、(b) 碱解氮、(c) P、(d) 速效磷散点图

Fig. 5 Scatterplot of available selenium with (a) N, (b) alkali-hydrolyzable N, (c) P and (d) available P. (a) Correlation between available selenium and nitrogen content; (b) Correlation between available selenium and alkali-hydrolyzable N content; (c) Correlation between available selenium and phosphorus content; d) Correlation between available selenium and available phosphorus content. Soil available selenium is positively correlated with N, P, alkali-hydrolyzable N and available P.

表 5　土壤有效硒和 CEC 与氮、磷等指标相关关系

Table 5　Correlation between soil available selenium and CEC and N, P and other indicators

指标	样品数量	氮	磷	有机质	碱解氮	有效磷	速效钾	有效硒
有效硒	1587	0.591**	0.406**	0.528**	0.538**	0.385**	0.500**	1
CEC	130	0.749**	0.649**	0.785**	0.601**	0.383**	0.431**	0.446**

注:“**”表示在置信度(双测)为 0.01 时,相关性是显著的。

5　结论

本文对西藏自治区隆子县土壤硒含量地球化学特征进行分析,探讨土壤硒和有效硒含量的主要影响因素。结果表明:①研究区表层土壤硒含量范围值为 0.14~1.51mg/kg,中位数为 0.44mg/kg,高于中国表层土壤和西藏土壤硒中位数含量,土壤硒含量大于 0.4mg/kg 为界限值,研究区总面积的 77.25%的土壤符合富硒土壤划定标准,富硒土壤资源丰富,且集中连片分布,表层土壤中有效硒含量占土壤全硒含量的 0.21%~5.79%之间;②研究区土壤硒含量影响因素主要为成土母质,特别是涅如组(T_3n)和日当组(J_1r)地层中发育的绢云母板岩和页岩中硒含量高,土地利用类型对硒含量及分布影响较小,土壤有机质、pH 值、TFe_2O_3、大量养分、CEC 等土壤理化性质对全硒含量影响有限,但可以显著提高土壤硒的生物有效性;③土壤垂向剖面研究发现,土壤硒含量除了受成土母质控制外,还受淋溶、生物累积等表生富集综合作用有关。

本文仅讨论了西藏自治区隆子县土壤硒含量特征及影响因素,以期为富硒土地资源开发利用提供地质依据。但农作物对硒的吸收过程是一个非常复杂的生物地球化学过程,且受多种因素的综合影响,因此,今后应进一步加强土壤-作物系统中硒含量特征及迁移转化研究。

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Geochemical Characteristics and Influencing Factors of Soil Selenium in Longzi County, Tibet Autonomous Region

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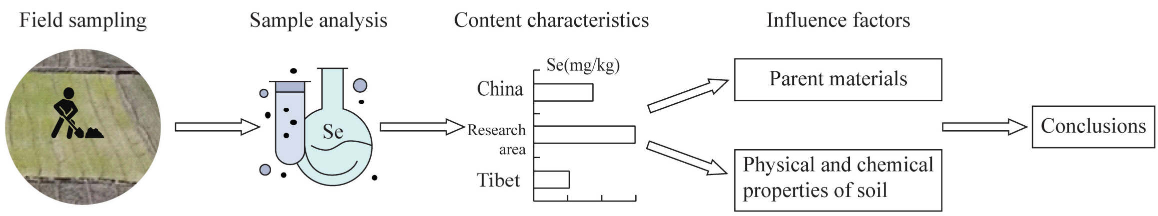
HIGHLIGHTS

(1) The soil Se content in the study area ranges from 0.14 to 1.51mg/kg, with a median of 0.44mg/kg, which is significantly higher than the average of surface soil Se content in Tibet and China.
(2) The soil Se content is closely related to the geological background and controlled by the black rock system of Neru and Ridang Formations.
(3) Soil organic matter, N, P, alkali-hydrolyzable N, available P, available K, and CEC content affect soil availability.



ABSTRACT

BACKGROUND: Selenium (Se) is one of the essential trace elements in the human body, which has many biological functions. Insufficient or excessive intake of Se will cause a series of diseases. The trace element Se in the human or animal body cannot be synthesized by itself, but can only be supplemented from external food. Se in food, especially in plant food, mainly comes from soil. Therefore, Se in soil is closely related to human health and animal growth. China is a country lacking in soil Se content, especially in Tibet. The background value of soil Se in Tibet is significantly lower than that of surface soil in China. Therefore, local diseases such as Kashin-Beck disease are common in some areas of Tibet due to long-term insufficient intake of selenium. It is of great significance to investigate the distribution characteristic of soil Se content, delineate the distribution area of selenium-enriched soil resources and determine the influencing factors of soil Se content for promoting the development and utilization of selenium-enriched land resources, develop Se-enriched industries and prevent local diseases. This will also provide reference data for the research of soil Se background value.

OBJECTIVES: In recent years, it has been a hot topic to investigate the content of Se in soil, to delineate selenium-enriched soil resources and to develop and utilize them. Tibet is the main part of the Qinghai—Tibet Plateau, which has complex and diverse soil parent materials and soil forming processes, forming unique alpine soil types. In addition, Tibet is one of the areas with the least influence of human activities and is the ideal place for environmental geochemistry research. However, due to many factors such as natural geographical location and climate, the research data of soil element geochemistry in Tibet is very limited, and research data of soil Se is rare. Thus, the characteristics, distribution and influencing factors of soil Se content in the study area were studied, to provide a basis for the exploitation and utilization of selenium-enriched land resources, the development of selenium-enriched industry and the prevention of endemic diseases in the frontier ethnic areas of the plateau.

METHODS: The collection, processing and analysis of samples of surface soil, vertical profile and rock profile were carried out. The samples were collected from the key farming area of Longzi County, Shannan, Tibet Autonomous Region. The surface soil samples were collected in a grid pattern from the third national land survey map spot. The soil sampling points were mainly arranged on agricultural plots, with an average sampling density of 7.9 points/km^2. A total of 1587 surface soil samples were collected, with a study area of 200km^2. The sampling method for surface soil samples was determined according to the actual plot shape. When the plot was square, "X" type sampling was adopted, and when the plot was rectangular, "S" type sampling was adopted. When sampling cultivated land, 5 sub-sampling points were equally combined into 1 sample; for grassland and woodland sampling, 3-4 sub-sampling points were equally combined into one sample. The samples collected at each sub-sampling point were crushed, small stones, roots and other sundries picked out, and after fully mixing, more than 1000g samples reserved and put into sample bags by quartering method. In the study area, 10 vertical soil profiles were set up, and the sampling interval was 1 sample/20cm. The depth of all the profiles was 160cm except for the profile CM01, which was 140cm deep. In addition, a rock profile was set in the study area, and fresh rock samples were collected. The same kind of rock was collected in a multi-point mode and combined into a sample, with the sample weight of 300g. The surface soil samples, and vertical profile samples collected were naturally dried without pollution, and sieved by -10 mesh nylon sieve, then divided by quartering method, weighed and put into sample bottles and sent to laboratory for analysis. Soil samples were analyzed for Se, available Se, organic matter, pH, N, P, available N, available P, available K, etc. Rock samples were analyzed for Se. The contents of Se and available Se were determined by atomic fluorescence spectrometry (AFS), organic matter. Available nitrogen and cation exchange capacity (CEC) were determined by volumetric method (VOL), pH value was determined by ion selective electrode method (ISE), N content was determined by elemental analyzer method (EA), and available P, available K, P and TFe_2O_3 were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). The detection limit, accuracy, precision and reporting rate of the analytical method adopted all met the specification requirements, and the sample analysis quality was reliable.

RESULTS: The results of the content of Se in soil and its influence factors, showed that: (1) The Se content in the topsoil of the study area ranged from 0.14 to 1.51mg/kg, with a median of 0.44mg/kg, which was 2.9 times as high as the average value of Tibet (0.15mg/kg) and 1.5 times as high as the average value of China (0.26 mg/kg). The content of available Se in the topsoil ranged from 0.8 to 26.8μg/kg, with a median of 9.2μg/kg. The content of available Se in topsoil was 0.21%-5.79% of total Se. (2) Se-enriched (Se≥0.4mg/kg) soil resource area was 154.53km^2, which accounted for 77.25% of the total area. Se-enriched soil was mainly distributed in Longzi Town and Ridang Town. There was no excess or deficiency of soil Se in the study area, which indicated that Se-enriched soil was continuous and had the potential to develop Se-enriched soil resources. (3) The geological background was closely related to the Se content in the soil. The Se rich soil was mainly controlled by the distribution of the Nieru Formation (T_3n) and the Ridang Formation (J_1r). The median Se content in the soil developed from the Nieru Formation (T_3n) and the Ridang Formation (J_1r) was 0.44mg/kg and 0.41mg/kg, respectively. Analysis of Se content in rock samples showed that Se content ranged from 0.07 to 11.00mg/kg, with an average of 1.65mg/kg. Se content was high in sericite slate and shale, which further proved that Se-enriched soil was closely related to its parent rock. (4) Soil physical and chemical properties including organic matter, pH, TFe_2O_3 had no significant effect on soil Se content, but soil available Se was positively correlated with organic matter, pH, N, P, alkali-hydrolyzable N, available P, available K, CEC content. There was a positive correlation between the content of organic matter and the content of available Se ($R^2=0.2792$, $P<0.01$), and between the content of organic matter and the ratio of available Se to total Se ($R^2=0.2597$, $P<0.01$). There was a positive correlation between soil available Se and pH ($R^2=0.103$, $P<0.01$). According to the soil pH grading standard, the availability of Se increased gradually from acid to alkaline soil, but in strong alkaline soil, the availability began to decrease due to the methylation reaction of Se. There was a negative correlation between available Se and TFe_2O_3 ($R^2 = -0.346$, $P < 0.01$). In the study area, the content of soil available Se had significantly positive correlation with the content of N, P, alkali-hydrolyzable N, available P and available K, which indicated that the increase of N, P and K content could significantly improve the bioavailability of soil selenium, which had a certain theoretical significance for the artificial control of soil Se content. (5) 10 vertical soil profiles were constructed in different areas of the study area, and the depth of the other profiles was 160cm except for the CM01 profile, which was 140cm. In that vertical soil profile, the content of Se and available Se decreased with the increase of soil depth. The content of Se in the soil below 100cm was less than 0.4mg/kg, and the content of available Se in the soil at 160cm was 60% less than that in the surface soil.

CONCLUSIONS: The content of Se in the topsoil of the study area is high, and 77.25% of the study area is in line with the standard of Se-enriched soil. In that soil, the Se content is mainly affected by the parent materials, especially the sericite slate and shale in the Nieru Formation (T_3n) and Ridang Formation (J_1r). The land use type has little effect on Se content and distribution. Physical and chemical properties of the soil, such as organic matter, pH, N, P, available N, available P, available K and CEC, have little effect on total Se content, but soil available Se is significantly positively correlated with organic matter, pH, N, P, alkali-hydrolyzable N, available P, available K and CEC. Soil nutrient management can further improve bioavailability of soil selenium. Only the characteristics and influencing factors of soil Se content in Longzi County, Tibet Autonomous Region, were discussed, in order to provide a geological basis for the development and utilization of Se-enriched land resources. However, the process of Se uptake by crops is a very complex biogeochemical process, and is affected by many factors. Therefore, it is necessary to further strengthen research on the characteristics of Se content and its migration and transformation in soil-crop system.

KEY WORDS: soil selenium; geochemical characteristics; influencing factors; atomic fluorescence spectrometry; Longzi County in Tibet