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Concentração de vanádio nas misturas de sal mineral utilizadas na suplementação de bovinos

Vanadium concentration in mineral salt mixtures used as supplementation in bovines

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Resumo: O comércio de suplementos minerais para bovinos no Brasil cresceu muito desde a última década. Muito embora seja necessária a utilização de matérias primas sem contaminantes, é possivel que alguns fabricantes ainda utilizem fontes de fósforo mais baratas. Essa situação pode veicular metais pesados na mistura mineral pronta, o que, em médio prazo, pode intoxicar os animais. Por essa razão, foi mensurada a concentração de Vanádio nas amostras de misturas de sal mineral usadas na suplementação de gado de corte nos estados do Paraná, Brasil. A concentração de vanádio foi determinada pela indução da espectrometria acoplada à emissão de plasma atômico. Das 22 amostras analisadas, 17 tinham valores maiores que 50 ppm (variando entre 66 e 128 ppm), a concentração máxima recomendada pelo Conselho Nacional de Pesquisa e pela Associação Americana de Controle Oficial de Alimentação. Esses resultados mostram a necessidade de um monitoramento industrial cuidadoso, porque algumas misturas de minerais contém quantidade suficiente de vanádio para causar intoxicação nos animais.

Termos para indexação: animais, intoxicação, misturas de minerais, monitoramento industrial.

Abstract: The commercialization of mineral supplements for cattle in Brazil has grown a lot since the last decade. Although it is necessary to use raw materials without contaminants, it is possible that some manufacturers still use cheaper sources of phosphorus. This situation can serve heavy metals in the ready mineral mixture, which in the medium term, can poison animals. For this reason, we measured vanadium concentrations in samples of mineral mixtures used in cattle feed. Vanadium concentration was determined by inductively coupled plasma atomic emission spectrometry. Of the 22 analyzed samples, 17 had values greater than 50 ppm (ranging between 66 to 128 ppm), which is the maximum concentration recommended by the National Research Council and the Association of American Feed Control Officials Incorporated. These findings show the necessity for careful industrial monitoring because some mineral mixtures contain sufficient vanadium to cause toxicity in animals.

Index terms: animals, industrial monitoring, mineral mixtures, toxicity.



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Introduction

The increasing price of raw materials, which make up a part of the mineral salt mixtures provided for animal consumption in Brazil, is the main reason why mineral mixture industries are being forced to consider reducing costs, with the aim of winning markets and guaranteeing their future business.

Because of this, many industries have used raw materials sources that are less expensive, some of them without the adjusted quality to compose the mineral mixtures.

In this aspect it is believed that some new mineral formulations can be contaminated by toxic elements, many of these being heavy metals and radioactive substances. Cheap sources of raw material could therefore be the origin of this problem. For this reason an investigative research was initiated with the intention of evaluating the level of pollutants in mineral formulations used in Brazilian cattle production, where today there are approximately 5.500 different mineral mixtures being sold throughout the Brazilian national market (MARÇAL et al., 2015).

The main goal of the present research is to investigate the xenobiotic presence in some different mineral supplements produced in Brazil. The investigative process occurred throughout laboratory analysis to quantify pollutants that can be attached to macro- and micromineral elements present in mineral formulations given to animal feed.

Vanadium was the element chosen for the study, which is considered for many specialists to be an inorganic element of great risk to cattle consumption (FRANK et al., 1996; MCCRINDLE et al., 2001; GUMMOW et al., 2006). The element has high toxicity (AAFCOI, 1993) with possible animal vehiculation through the ingestion of contaminated mineral formulations (ALLEN, 1992; NRC, 1996; MARÇAL et al., 2001).

Material and Methods

The samples were collected directly from the main commercial resellers in different cities, where there were many cattle. Each sample weighed about 200 grams, and noted the manufacturing date, expiry period and batch number. At harvest the containers were sealed, with original factory. Samples were paid an identification code to prevent the disclosure of the brand and manufacturer, with respect to research ethics. The samples were placed in sealed plastic bags and then sent to be analyzed in the National Commission of Nuclear Energy (CNEN) Laboratory at Poços de Caldas, Minas Gerais, Brazil. The samples were initially dried at 110°C for two hours,

dissolved in nitric acid and then the vanadium was extracted with pyrrolidine ammonia dithiocarbonate (APCD) p.a. at pH 2.3 \pm 0.1. Vanadium content was determined by spectrometry of atomic emission plasma induction coupled at 220.3 nm using a Jarrel-Ash model 975 spectrometer. Analysis methodology was made based on ASTM (1980). Limit of determination of the method was 0.5 ppm. Statistical analyses were made with the

SAS/Basic Program, as described in SAS PROCEDURES GUIDE (SAS, 1990). **RESULTS**

The vanadium concentrations in 22 different samples of mineral mix of Brazil are presented in Table 1. Graphical presentation of the results is in Figure 1.

From the data set: Average: 73.22727; SD: 25.00752; Coefficient of variation: 34.15055; Median: 70.875.

Table 1: Values of vanadium concentrations founded in Brazil

Sample number	Sample code	Lab code	Values of Vanadium (ppm)
01	VPR 39 80/12	22767	87 ± 4,35
02	VPR 52 80/25	22768	$71 \pm 3,55$
03	VPR 50 80/23	22769	$31 \pm 1,55$
04	VPR 47 80/20	22770	$85 \pm 4,25$
05	VPR 45 80/18	22771	$68 \pm 3,4$
06	VPR 34 80/17	22772	100 ± 5
07	VPR 33 80/16	22773	$82 \pm 4,1$
08	VPR 51 80/14	22774	$45 \pm 2,25$
09	VPR 10 65/10	22775	$67 \pm 3,35$
10	VPR 54 80/27	22776	$66 \pm 3,3$
11	VPR 36 80/19	22777	$67 \pm 3,35$
12	VPR 42 80/15	22778	$102 \pm 5,1$
13	VPR 29 80/12	22779	$38 \pm 1,9$
14	VPR 08 65/18	22780	$32 \pm 1,6$
15	VPR 40 80/13	22781	$64 \pm 3,2$
16	VPR 41 80/14	22782	$64 \pm 3,2$
17	VPR 48 80/21	22783	$128 \pm 6,4$
18	VPR 38 80/11	22784	$46 \pm 2,3$
19	VPR 32 80/05	22785	$95 \pm 4,75$
20	VPR 09 65/09	22786	$97 \pm 4,85$
21	VPR 37 80/10	22787	$95 \pm 4,75$
22	VPR 31 80/04	22788	$81 \pm 4,05$



Values of vanadium concentrations founded in Brazil

Figure 1: Average values (N=22) for vanadium concentrations in mineral salt in Brazil correlated with reference values from NRC (1996)

In the graph: black line is the median (50 % of the data is above the line / 50% below). Red line is the maximum acceptable limit of 50 ppm, according to the NRC (1996).

Discussion

Cattle nutrition has been improved in many countries over the past 30 years. This activity has become complex and expressive progress in the field of the mineral supplements has been achieved. In Brazil, the subject of sanitary control in animal feeding has received great attention and today seems to be increasingly strengthened due to specialist participation, with practical objectives (MARÇAL et al., 2015). Within this aspect, investigating the presence of pollutants in mineral mixtures is a type of research unique in its nature in the country as a whole.

Due to the high number of mineral formulations sold around the country (5.500 different brands), samples of mineral mixtures were collected in a number of manufacturing cities. The approach was to work in some cities that hold a significant number of cattle under their effective control. This study was carried out in these places because of established levels of cooperation in each location. Samples at harvest were coded, avoiding inconvenience to reviewers.

Results show that 77% of samples exceeded the maximum limit of 50 ppm for vanadium concentration as proposed by the Association of American Feed Control Officials Incorporated (2001) and by the NATIONAL RESEARCH COUNCIL (1996).

It is important to remember that vanadium appears to exert its toxic effect through inhibition of enzymes and cell damage from lysis. Besides, numerous reviews on vanadium toxicity are available (SJOBERG, 1950; STOKINGER, 1955, 1963; FAULKNER-HUDSON, 1964; LILLIE, 1970; NATIONAL RESEARCH COUNCIL, 1974). Vanadium appears to exert its toxic effect through inhibition of enzymes (Underwood, 1977) and cell damage from lysis (WATERS et al., 1975). Vanadate has been found to inhibit (Na, K)-ATrase (Cantley et al., 1977, 1978; Nechay and Saunders, 1978; Goodno, 1979; Nieder et al., 1979) and activate cardiac adenylate cyclase (GRUPP et al., 1979). Signs of toxicosis in calves and lambs include diarrhea, depressed growth and performance, ataxia, and mortality.

Vanadium toxicosis has not been studied as extensively as many of the other minerals, although the recent recognition of high concentrations in some phosphates, coals, and petroleum products has increased interest in the movement of the element from the environment to animals and man.

It is most probable that in this research vanadium as well as lead comes from common sources of macro-elements, such as phosphorus (Marçal et al., 2001), which represent the highest costs in mineral salt composition (MARÇAL et al., 2015). If mineral salt mixture industries do not raise the level of their quality concerns related to the aspect of raw material purity, increasing commercialization will ease the presence of more pollutants in animal feed. This in turn can threaten human health through the contaminated food chain. The aspect of raw materials purity used in supplements for animal feed should be one of the main subjects of marketing. A great part of this is due to the fact that the ecological label induces buyers to acquire certain products whose production essence demonstrates concern with the environment and the preservation of the meat and milk quality.

Nowadays with the modern technology, it is expected that the National Research Council as well as the American Association of Feed Control, should revise these reference values so that less fluctuation values would be found and also will be a concern that no value of vanadium should be found in any analyzed sample.

The next phase of our studies will be to investigate possible subclinical effects of vanadium toxicity in cattle receiving mineral mixes with the highest vanadium content. Possible interferences in the reproductive cycles of the cows and decreased levels of performance will be the main effects sought as referred to by & **OEHME STUART** (1982), MCDOWELL (1985), MARACEK et al. (1998) and MARÇAL et al. (2003). This can be one of the reasons that can influence the values of birth per breeding that is as low as 22% in Brazil.

Finally, if mineral salt mixture industries do not improve their quality concerns related to the aspect of raw material purity, the increasing commercialization will easy the presence of more pollutants in the animal feeding. This in turn will threat man health, through the contaminated food chain compromising the quality of meat and milk.

Conclusions

The results analysis allow us the following conclusions:

1st) From the 22 analyzed formulations, only five samples presented results below
50 ppm, considered the maximum limit attributed by National Research Council (1996), representing 23% of the analyzed mineral supplements;

2st) In 17 samples, vanadium concentration was greater than 50 ppm, the maximum limit attributed by NATIONAL RESEARCH COUNCIL (1996). This represents 77% of the analyzed mineral formulations;

REFERENCES

AAFCOI, Official guidelines for contaminant levels permitted in mineral feed ingredients. Association of American Feed Control Officials Incorporated. Indiana, 19, pp. 292-293, 2001.

ALLEN, J.D. 1992. *Minerals in animal feed.* Industr. Miner, 292, pp. 35-39. AMERICAN SOCIETY FOR TESTING AND MATERIALS. *Water.* In: Annual book of ASTM Standards. Philadelphia: ASTM, 1980, p. 450-464.

BERG, L.R. 1963. Evidence of vanadium toxicity resulting from the use of certain commercial phosphorus supplements in chick rations. **Poult. Sci.**, 42:766.

CANTLEY, L.C, JR., AND P. AISEN. 1979. *The fate of cytoplasmic vanadium, implications on (Na, K)-ATPase inhibition.* J. Biol. Chem., 254:1781. CANTLEY, L.C, JR., L. JOSEPHSON, R. WARNER, M. YANAGISAWA, C. LECHENE, AND G. GUIDOTTI. 1977. Vanadate is a potent (Na, K)-ATPase inhibitor found in atp derived from muscle. J. Biol. Chem., 252:7421.

CANTLEY. L.C, JR., L.G. CANTLEY, AND L. JOSEPHSON. 1978. A characterization of vanadate interactions with the (Na, K)-ATPase mechanistic and regulatory implications. J. Biol. Chem., 253:7361.

COMAR, D., AND F. CHEVALLIER. 1967. Concentration du vanadium chez le rat et son influence sur la synthese du cholesterol, etudiees par la technique de radioactivation neutronique et la methode 'equilibre isotopique. **Bull. Soc. Chim. Biol.**, 49:1357.

FAULKNER-HUDSON,T.G.1964.Vanadium.ToxicologyandBiologicalSignificance.New York:ElsevierPublishingCo.Co.Co.Co.

FRANK, A., MADEJ, A., GALGAN, V., PETERSSON, L.R. Vanadium poisoning of cattle with basic slag. concentrations in tissues from poisoned animals and from a reference, slaughterhouse material. **Sci Total Environ**. 1996 Mar 1; 181(1):73-92.

GOLDSCHMIDT, V.M. 1958. *Vanadium*. In A. MUIR (ed.). Geochemistry. Clarendon Press, Oxford.

GOODNO, C.C. 1979. Inhibition of myosin ATPase by vanadate ion. Proc. Natl. Acad. Sci., 76:2620.

GRUPP. G.I. GRUPP, C.L. JOHNSON, E.T. WALLICK, AND A. SCHWARTZ. 1979. *Effect of vanadate on cardiac contraction and adenylate cyclase*. Biochem. Biophys. Res. Commun. 88:440.

GUMMOW, B., BOTHA, C.J., WILLIAMS, M.C. Chronic vanadium poisoning in calves and its treatment with calcium disodium ethylenediaminetetraacetate. Vet Res Commun., 2006 Oct; 30(7):807-22. LILLIE, R.J. 1970. *Vanadium*. In Air Pollutants Affecting the Performance of Domestic Animals—A Literature Review. Agric. Handb. No. 380. U.S. Department of Agriculture, Washington, D.C.

MARACEK, I; LAZAR, L.; DIETZOVA, I.; KORENEKOVA, B.; CHOMA, J.; DAVID, V. 1998. *Residues of heavy metals in cow reproductive organs and morbidity of cattle in the fallout region of a metallurgical plant.* Vet. Med. – Czech, 43, 9, p. 283-287.

MARÇAL, W. S.; GASTE, L.; LIBONI, M.; PARDO, P. E.; NASCIMENTO, M.R.; HISASI, C. 2001. Concentration of lead in mineral salt mixtures used as supplements in cattle food. Experimenthal and Toxicologic Pathology, Jena 53, 7-9.

MARÇAL, W.S.; PARDO, P.E.; NASCIMENTO, M.R.L.; VERAS, E.B.; MORENO, A. M. Levels of lead in mineral salt commercial mixtures for beef cattle. **Journal of Veterinary Science**, Korea, v.4, n.3, p. 235-238, 2003.

MARÇAL, W.S., NASCIMENTO, M.R.L., MENCK, M.F. Toxic levels of zinc in mineral salt mixtures used in beef cattle supplementation. **Veterinary Science in the tropics,** v.18, n.1, p.43-46, 2015.

MCCRINDLE, C.M., MOKANTLA, E., DUNCAN, N. *Peracute vanadium toxicity in cattle grazing near a vanadium mine.* J. Environ Monit. 2001 Dec., 3(6):580-2.

McDOWELL, L.R. *Nutrition of grazing ruminants in warm climates.* Orlando: Academic Press, 1985.

NATIONAL RESEARCH COUNCIL. Vanadium. Washington, D.C.: National Academy of Sciences, 1974.

NATIONAL RESEARCH COUNCIL. Nutrient requirements of beef cattle. National Research Council. Subcommittee on Mineral Toxicity in Animals. Washington D. C.: National Academy of Sciences, 1996. NECHAY. B.R., AND J.P. SAUNDERS. 1978. Inhibition by vanadium of sodium and potassium dependent adenosinetriphosphatase derived from animal and human tissues. J. Environ. **Pathol. Toxicol.** 2:247.

NIEDER, G.L., C.N. CORDER, AND P. A. CULP. 1979. *The effect of vanadate on human kidney potassium dependent phosphatase*. Arch. Pharm. 307:191.

SAS (1990): SAS procedures guide: version 6. 3rd ed Cary, SAS Institute. p. 705.

SJDBERG, S.G. 1950. Vanadium pentoxide dust. A clinical and experimental investigation on its effect after inhalation. Acta Med. Scand. 138:238.

STOKINGER, H.E. 1955. Organic beryllium and vanadium dusts. A review, Arch. Ind. Health. 12:675.

STOKINGER, H.E. 1963. *Vanadium*. In F. A. Patty, ed. Industrial Hygiene and Toxicology, vol. II. Toxicology, 2nd ed. Interscience Publishers, New York.

STUART, L.D., F.V. OEHME. 1982: Environmental factors bovine and porcine abortion. **Veterinary and Human Toxicology**, 24, 435-41.

UNDERWOOD. E.J. 1977. Trace Elements in Human and Animal Nutrition, 4th ed., pp. 416-424. Academic Press, New York.

WATERS, M.D., D.E. GARDNER, C. ARANYI, AND D.L. COFFIN. 1975. *Metal toxicity for rabbit alveolar macrophages in vitro*. **Environ. Res**. 9:32.