Heavy metals exist in the soil in immobile (sulphides, phosphates, silicates, etc.) and mobile forms. The mobile forms occur with the exchange processes in the soil and with the changing composition, pH, etc. of soil. Determination of the mobile forms of heavy metals is important for understanding their migration patterns in the soil and their uptake by plants. The aim of this work was to compare some determination methods of immobile and mobile forms of heavy metals.

The total content of Cd, Cu, and Pb was determined in aqua regia (mixture of HCl, HNO₃, and H₂O₂) and 2M HNO₃ extracts by boiling. The results obtained by both methods show a good correlation.

The content of the mobile form of heavy metals depends on the nature of metal ion, the nature of extractant and pH. The mobile forms of Cd, Cu and Pb were determined by using ammonium nitrate, ammonium acetate (pH 7 and 4.8), 0.1M HCl and 0.05 M NH₄–EDTA (pH 7). The smallest amounts were extracted with ammonium salt solutions. The content of heavy metals extracted with ammonium acetate (pH 7) was higher than that extracted with ammonium acetate (pH 4.8). Even greater contents of heavy metals were extracted with 0.1 HCl. 0.05 M NH₄–EDTA (pH 7) is capable of extracting from the soil not only the heavy metals participating in the exchange processes, but also the heavy metals in carbonates and organic complexes (bound). A comparison of the mobile forms of heavy metals extracted from clean and highly polluted soils has revealed that in the polluted soils the greater portion of heavy metals exists in a mobile form.

**Key words:** heavy metals, soil analysis, mobility of metals, chemical extraction

**INTRODUCTION**

Analysis of heavy metals in the soil takes a few forms and they depend on the purpose of the analysis. Firstly, it is the determination of the ‘total’ element contents in the soil by the methods that use solid samples, such as X-ray fluorescence spectrometry (XRF), DC arc optical emission spectrometry (DCAOES), neutron activation analysis (NAA), and glow discharge mass spectrometry (GDMS), or by various methods where solutions prepared by acid dissolution involving hydrofluoric acid or by fusion (LiBO₂) / dissolution procedures are used.

Secondly, analysis of strong acid digests of soil is carried out to assess the extent of heavy metal pollution accumulated in topsoil and provide an assessment of the long-term potential toxicity effects of pollution as well as of long-term potential deficiency situations where pollutant is not the issue. Since most pollutant inputs are not silicate-bound, a ‘pseudototal’ analysis of strong acid digests, not involving dissolution of silicates by hydrofluoric acid, is sufficient. This type of analysis using aqua regia digestion is already the subject of an approved German DIN procedure and an ISO method (ISO : 11466). This aqua regia digestion method has been widely adopted in Europe. The 2 M HNO₃ digestion is also used for ‘pseudototal’ trace element analysis in the Integrated Monitoring by countries of the Baltic Sea region (UN/ECE..., 1998). While this is technically an extraction procedure (extraction by strong acids), it is normally carried out on soil material ground to < 150 µm and is thus poorly related to the field soil situation and to the problems of element mobility or availability to crop plants.

Next, for understanding the chemistry of heavy metals in their interaction with other soil compo-
nents such as clay minerals, organic matter and soil solution, or to assess their mobility and retention as well as their availability to plants, the usual approach is to use selective chemical extraction (Ure, 1996). Soluble, exchangeable and chelated forms of metal in the soils are the labile fractions available for plants. Soil extraction is the method of isolating functionally defined forms of metal. The notion "form of heavy metal" defines the function of matter in the soil, as, for example, 'plant available form', 'exchangeable cations' or 'labile form'. The forms defined in this way are not narrow individual chemical forms but may embrace a number of chemical substances that share a common function and are all available to plants. Although their precise chemical nature may be indeterminate, the function is quite precise. This kind of definition has been used in soil and agricultural laboratories for half a century. Various extractants are used in different laboratories, for example, non-buffered neutral salts (0.1 M natrium nitrate, 0.01 M calcium chloride, 1 M ammonium nitrate), buffer ammonium acetate (pH 7 and 4.8), diluted acids (2.5% acetic acid, 0.1 M hydrochloric acid), complexing extractants 0.05 M EDTA and 0.005 M DTPA). In Germany, a combination of 1 M ammonium nitrate or 0.1 M calcium chloride and 0.025 M Natrium-EDTA is widely used (Podlesakova, 2001). The extraction methods outlined above have been widely and successfully applied in the study of nutrient element deficiency in agricultural crops and animals as well as in environmental pollution analysis.

Also, sequential extraction procedures are often used in soil studies to determine the forms or phases of elements. The development and use of sequential extraction schemes started in the early 1980s with the primary objective of evaluating the metal fractions available to plants and the environmentally accessible trace metals. Sequential extraction schemes such as those of Tessier et al. (Tessier et al., 1979), McLaren and Crawford (McLaren and Crawford, 1978), and Shuman (1985) (McGrath, 1996) can improve our understanding of physico-chemical associations with soil particles, mobility and plant availability for each element. Sequential extraction provides a detailed information allowing the differentiation among several association forms. Usually, the fractions considered are as follows: exchangeable, organically complexed, carbonate bound, iron and manganese hydroxides linked and residual fractions. The total amount measurements show the heavy metal quantity in the soil, but this may differ from plant-available forms (Symeonides, McRae, 1977). Therefore, the available mobile forms should also be evaluated (Maiz et al., 2000). The main purpose of this study is comparison of determination methods of some cadmium, lead and copper 'pseudototal' and mobile forms. The other aim is to compare the quantities of mobile forms of heavy metals in the samples of non-contaminated soils from Lithuania and soils contaminated with zinc and lead from mining areas in North England.

**MATERIALS AND METHODS**

**Sampling**

Five samples of soil surface (0–10 cm) were randomly collected following the "envelope" pattern from 3 different sites in Balbieriškis district, Lithuania in November 2000. The microdistrict of Balbieriškis–Simnas is located in a limnoglacial plain on the left side of the Nemunas River in the Lithuanian midland (Basalykas, 1965; Atlas..., 1978). There are various pedogenetic rocks, moraine loam predominate. Also, there are some plots of limnoglacial loam and clay. Some podzolic sands are found in the valley of the Nemunas River. These locations were not affected by any anthropogenic sources of pollution. Samples of alluvial sand, moraine clay and loam soils were collected for the analysis.

Other eight subsoil samples were collected in May 2000 from the metal-contaminated alluvial deposits formed in the late 19th and the first half of the 20th century in the Tyne River in North England. The Tyne Basin (the area is 2927 km²) occupies the North Pennine area where zinc and lead mines are located. The quantities of lead, zinc, copper, which have been produced since Roman times reach 1.6 · 10⁶ t, 2.9 · 10⁵ t and 1.6 · 10³ t, respectively. Mining production reached the maximum in the mid-nineteenth century. Imperfect ore extraction, sorting and dressing technologies resulted in a large deposition of heavy metal-bearing minerals into the Tyne Basin. The contemporary sediments of the Tyne River and alluvial deposits from mining activities times mainly contain quartz and sandstone. Chemical investigations of lead-, zinc-, cadmium- and copper-bearing river sediment suggests that these metals are associated with an iron/manganese oxyhydroxide phase (Hudson-Edwards et al., 1996).

The soil samples were air-dried, ground to pass through a 2-mm aluminium mesh and stored at room temperature in polyethylene bags.

**Soil properties and total metal contents**

Soil pH was determined in a soil and 0.01 M calcium chloride (1:2.5) suspension (Methods..., 1996).
with pH-meter 3020. Organic matter content determination was carried out following the international standard method ISO 10694. The pH values were close to neutral and ranged from 5.66 to 6.99. Organic matter values ranged from 1.07% to 2.6%.

Total cadmium, copper and lead contents were determined after digestion with both aqua regia (1 g soil : 2.5 ml nitric acid, 7.5 ml hydrochloric acid and 0.5 ml 30% hydrogen peroxide) (Kilburn, 2000) and 2 M nitric acid (5 g soil : 100 ml concentrated nitric acid) (UN/ECE... , 1998). The amounts of elements were determined by atomic absorption spectrometry (AAS).

The ranges and the mean values of the characteristics of soils and total heavy metal contents are given in Table 1.

### Results and Discussion

#### Total heavy metal contents

The total concentrations (range and mean values) of cadmium, copper and lead in Lithuanian and English soils are listed in Table 1. The critical total soil concentration is defined as the range of values above which toxicity is considered possible. Kabata-Pendias and Pendias considered the following upper values of the critical soil data: 3–8 mg/kg cadmium, 60–125 mg/kg copper, and 100–400 mg/kg lead (Kabata-Pendias, Pendias, 1984). Different values are accepted in Lithuania: 3–5 mg/kg cadmium, 40 mg/kg copper, and 32 mg/kg lead (LAND 20–2001). One can see that the natural background concentration of all metals is present in all Lithuanian soils. In British soils the concentration of cadmium and lead was above the upper critical level, while copper showed a low concentration.

Figure shows a correlation between heavy metal contents in aqua regia and 2 M nitric acid. For lead, a highly significant correlation between both methods was found. Also for cadmium and copper significant correlations were determined. In some cases nitric acid extracted the same amounts of heavy metals as did aqua regia, but in most cases less or more. As affirmed by Beckett, aqua regia digestion has no advantage over the nitric acid digestion in spite of hydrogen peroxide which oxidizes organic matter (Beckett, 1989). The aqua regia digestion is

### Table 1. Some Lithuanian and English soil properties and ‘total’ heavy metal contents

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH (CaCl&lt;sub&gt;2&lt;/sub&gt;)</th>
<th>C (%)</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aqua regia</td>
<td>HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Aqua regia</td>
</tr>
<tr>
<td>Lithuanian</td>
<td>5.66–6.88</td>
<td>1.14–2.11</td>
<td>0.13–1.91</td>
<td>-</td>
<td>3.68–9.22</td>
</tr>
<tr>
<td>Range</td>
<td>(6.07)</td>
<td>(1.72)</td>
<td>(1.1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>English</td>
<td>6–6.99</td>
<td>1.07–2.06</td>
<td>2.36–6.2</td>
<td>2.95–5.35</td>
<td>5.25–12.84</td>
</tr>
<tr>
<td>Range</td>
<td>(6.75)</td>
<td>(1.91)</td>
<td>(3.98)</td>
<td>(4.01)</td>
<td>(9.41)</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Critical level</td>
<td>Lithuanian</td>
<td>3–5</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>English</td>
<td>3–8</td>
<td>60–125</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>British</td>
<td>3–82</td>
<td>32</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### The extractable heavy metal contents

The extractable heavy metal amounts were determined in various chemical extractants. The amount of the extracted element depends on the nature of the extractant, soil/extractant ratio, extraction time and methodology. The extraction methods were selected according to the British and American literature (Methods..., 1996; The analysis..., 1986). The used extractants and extraction conditions are presented in Table 2. After extraction soil samples were filtered through a 125 mm Whatman No. 40 filter paper and examined by AAS ATI UNICAM 929.

### Table 2. Extractants used for soil testing

<table>
<thead>
<tr>
<th>Extractant</th>
<th>Soil/extractant ratio g : ml</th>
<th>Extraction time (h)</th>
<th>Main analytes [literature]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M NH₄NO₃</td>
<td>10 : 100</td>
<td>0.5</td>
<td>Mg [23], K [13], Cd, Pb [25]</td>
</tr>
<tr>
<td>1 M NH₄OAc (pH 7)</td>
<td>10 : 100</td>
<td>24</td>
<td>Mn [23], Cd, Pb [15]</td>
</tr>
<tr>
<td>1 M NH₄OAc (pH 4.8)</td>
<td>10 : 100</td>
<td>24</td>
<td>Zn [15], Cd, Cu, Pb</td>
</tr>
<tr>
<td>0.1 M HCl</td>
<td>2 : 20</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>0.05 M NH₄–EDTA</td>
<td>10 : 50</td>
<td>1</td>
<td>All [23]</td>
</tr>
</tbody>
</table>
Determination of heavy metal mobile forms by different extraction methods

Recommended for heavy metal content determination in soils polluted from anthropogenic sources (Beckett, 1989).

Extractable heavy metal contents in various extractants

Soil extractants listed in Table 2 were used to isolate and extract elements from particular soil phases. According to the concept of Viets, elements occur in soluble, exchangeable, organically complexed, secondary (carbonates, hydroxides of iron and manganese, sulphides, etc.) and primary mineral soil ‘pools’ of different solubility (Viets, 1962). Reagents of different strength can access one or a few ‘pools’. The experiment results for cadmium, copper and lead are shown in Table 3 as percentages of the different fractions with respect to the total amount in the soil aqua regia extract (Table 1). One can see that 1 M ammonium nitrate extracted the smallest heavy metal amounts, while 0.1 M hydrochloric acid extracted the biggest amounts.

The release of metal ions weakly bound electrostatically is promoted by ion exchange with cations such as ammonium and others (Ure, 1996). Ammonium salts of strong acids such as ammonium nitrate may be used as extractants for heavy metal exchangeable fraction. Results show that very small amounts of a heavy metal in the soils tested are in the exchangeable ‘pool’. The extractability follows the sequence Cd > Cu > Pb, which corresponds to the sequence of mobility. The amounts extracted were not proportional to total amounts in aqua regia for copper and lead, meanwhile a weak correlation for cadmium was found (Table 4). Nevertheless, Symeonides got a very good correlation between cadmium amounts in ammonium nitrate extract and in plants (Symeonides, McRae, 1977). Therefore, ammonium nitrate is a suitable extractant for plant-available cadmium determination. This reagent is not recommended for plant-available copper determination, because the latter is present in soil in organic complexes and ammonium nitrate doesn’t extract them (Symeonides, McRae, 1977).

The extractant’s pH has a considerable influence on extractable heavy metals. Soils in contact with 1 M ammonium acetate (pH 7) is perhaps the most preferred reagent for exchangeable metals because of its relatively high concentration and the metal complexing power of the acetate ion, which prevent readsoption or precipitation of released metal ions (Podlesakova et al., 2001). This reagent released bigger amounts of heavy metals than did ammonium nitrate (Table 3). The results for ammonium acetate (pH 7), presented in Table 4, show a good correlation between extracted and ‘total’ metal for cadmium and lead, however, almost no correlation for copper because of the same reason as for ammonium nitrate.

The extractant’s pH has a considerable influence on extractable heavy metals. Soils in contact with

![Graphs of metal amounts versus extractant pH](image-url)

Table 3. Heavy metal amounts (%) depending on ‘total’ amount

<table>
<thead>
<tr>
<th>Soil</th>
<th>Metal</th>
<th>1 M NH₄NO₃</th>
<th>1 M NH₄OAc (pH 7)</th>
<th>1 M NH₄OAc (pH 4.8)</th>
<th>0.1 M HCl</th>
<th>0.05 M NH₄– EDTA (pH 7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithuanian</td>
<td>Cd</td>
<td>4.36</td>
<td>5.43</td>
<td>–</td>
<td>30.83</td>
<td>–</td>
</tr>
<tr>
<td>English</td>
<td>Cd</td>
<td>4.0</td>
<td>18.23</td>
<td>49.96</td>
<td>61.83</td>
<td>40.79</td>
</tr>
<tr>
<td>Lithuanian</td>
<td>Cu</td>
<td>2.09</td>
<td>1.28</td>
<td>–</td>
<td>68.4</td>
<td>31.8</td>
</tr>
<tr>
<td>English</td>
<td>Cu</td>
<td>1.33</td>
<td>5.30</td>
<td>–</td>
<td>61.35</td>
<td>43.13</td>
</tr>
<tr>
<td>Lithuanian</td>
<td>Pb</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>27.6</td>
<td>21.41</td>
</tr>
<tr>
<td>English</td>
<td>Pb</td>
<td>0.07</td>
<td>1.49</td>
<td>22.59</td>
<td>39.61</td>
<td>42.78</td>
</tr>
</tbody>
</table>
1 M ammonium acetate (pH 7) are fairly effectively buffered at pH 7, the natural pH of the soil is as unlikely to influence the results as are extractions carried out at lower pH (Nielsen et al., 1986; Symeonides, McRae, 1977). Ammonium acetate (pH 4.8) releases not only exchangeable but also carbonate 'pool' (Ure, 1996). Therefore, this reagent extracts much bigger contents of heavy metals than does 1 M ammonium acetate (pH 7) (Table 3). The correlation between the extracted and the 'total' metal amount in ammonium acetate (pH 4.8) is better than that in ammonium acetate (pH 7) (Table 4), though a better correlation between metal amounts in ammonium acetate (pH 7) and in plants is found (Symeonides, McRae, 1977).

0.1 M hydrochloric acid releases heavy metals from many soil 'pools', e.g., exchangeable, organically complexed and secondary minerals (carbonates, oxides and hydroxides of iron and manganese) (Harmsen, 1977). Therefore, this reagent extracted the biggest amounts of heavy metal (Table 3). The extractability follows the sequence Cu > Cd > Pb. One can see that copper is the best extractable metal. This fact confirms the K. Harmsen’s proposition that copper in soil generally presents organically complexed and secondary mineral 'pools' (Harmsen, 1977). Hydrochloric acid is in full dissociation, does not oxidize metals and forms chelated complexes with cadmium. Therefore it is recommended for determination of some extractable heavy metals, especially cadmium (Lagerweft, 1971). Results of the experiment (Table 4) show an excellent correlation between the extractable and the total metal for cadmium and lead and a fairly good correlation for copper. Lagerweft (1971) obtained a good correlation between cadmium extracted with 0.1 M hydrochloric acid in soil and in plants. However, Symeonides (1977) found only a weakly perceptible correlation. Thus, the use of 0.1 M hydrochloric acid for plant-available heavy metal determination is rather limited.

Ammonium-EDTA forms strong complexes with numerous heavy metals. It releases heavy metals from soil exchangeable (Kabata-Pendias, Pendias, 1984) and organically complexed 'pools' (Podoleska et al., 2001; Singh et al., 1998). It also has an influence on heavy metals bound in carbonates and hydroxides of iron (Beckett, 1989). Therefore, a 0.05 M ammonium-EDTA (pH 7) extracts fairly large heavy metal amounts (Table 3). Heavy metal extractability depending on the metal-EDTA complex stability constant K follows the sequence Cu(K = 18.8) > Pb (K = 18) > Cd (K = 16.5) (Harmsen, 1977). It shows a close connection of copper and organic matter. Copper and lead, extracted with 0.05 M ammonium-EDTA (pH 7), strongly correlates with 'total' amounts. Cadmium is significantly correlated with total cadmium (Table 4). Jones (1973) found that the correlation of heavy metal extracted with ammonium-EDTA in soil and in plants is better than between the 'total' heavy metal amount and their amount in plants (Jones et al., 1973). Therefore, 0.05 M ammonium-EDTA is a widely used extractant for plant-available heavy metal determination in England and other countries (McGrath, Loveland, 1992).

Some authors ascertain that more easily extractable heavy metal amounts are in soils of anthropogenic contamination than in background concentration zones (Chlopecka et al., 1996; Harmsen, 1977). The results of this investigation approve this proposition (Table 3). The amount of extracted metal depends also on the origin of a soil contamination source. Cunningham et al. extracted bigger heavy metal amounts from soils polluted with mineral salts than from soils amended with sewage sludge containing corresponding amounts of heavy metals (Cunningham et al., 1975).

Choosing the extractant and the extraction method requires taking into account the aim of the investigation, the origin and 'pool' of the extractable element, soil type and contamination source. Comparison of the amounts of an element in the extractant and in plants is purposive in determination of plant-available heavy metal amounts.

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SUNKIOJØ METALØ JUDRIØJØ FORMØ NUSTATYMAS ÀAÎRIAIS EKSTRAHAVIMO METODAIS
Santrauka

Sunkieji metalai dirviojėje gali būti nejudrios (sulfīda, fosfāta, silikāta ir kt.) ir judrios formos, kuri atsiranda dirviojėje vykstant mainos procesams, kintant dirviojės sudėtis, pH ir kt. Judriuoju metalo forma nustatymas svarbus vertinant jo migraciją dirviojėje ir patekimą augalui. Darbo tikslas – palyginti kai kuriuos sunkiojų metalų bendrą ir judrą formą.

Bendri Cd, Cu ir Pb kiekiai nustatyti aqua regia (HCl, HNO₃ ir H₂O₂ mišiniai) ir 2M HNO₃ ekstraktuose jų nuostatas, kuriame atsiranda sunkiosios metalo formos. Gyvatės kiekiai padidėja ankstesnėje ekstrakcinėje faze. Jūsų jėga gali būti atliekama ekstrakcinėje faze, kurioje padidėjo sunkiosios metalo formos.

Sunkiojų metalų judriuosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosiosio